Effect of Nickel Oxide on Morphological and Electrical Properties of Manganese Oxide Nanostructured Thin Films

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Abstract: In this study, thin films of manganese oxide (Mn_3O_4) doped with nickel oxide (NiO) at different doping ratios (0, 1, 3, 5, and 7%) were prepared and deposited on glass slides at a temperature of 350°C using the chemical spray pyrolysis technique. Spectral analysis was performed, and a scanning electron microscope (SEM) was used. The SEM results show that the prepared films are spherical in shape, resembling cauliflower, and are irregular in size. This irregularity is due to the crystalline defects generated in the films. An Energy Dispersive Spectrometer (EDS) analysis was conducted to verify the components of the prepared thin films, which allowed for the determination of the weight and atomic ratios of the elements composing the films. Regarding the electrical measurements, conductivity, resistivity, the Hall coefficient, and charge carrier concentration were determined. We note that the prepared films exhibit p-type charge carriers and that the Hall effect increases with increasing doping ratios. The Hall coefficient values increase with doping ratios and reach their highest value at 3%, while the resistivity values peak at a doping ratio of 1%. The films show low conductivity overall, with the highest conductivity value observed at 7% doping. Similarly, the mobility increases with doping and attains its highest value at 7%.

1 INTRODUCTION

The advancement of nano science, an interdisciplinary field encompassing physics, chemistry, and material science, has recently been greatly aided by nanostructured thin films. [1], Manganese oxides are becoming one of the most potent transition metal oxides and diverse classes of functional materials that are having a key impact on science and technology [2], [3] , 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. 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 [4] , Manganese oxides, which are magnetic by nature, can form various crystal structures like MnO, Mn_2O_3, Mn_3O_4, and others, and exhibit various oxidation states of manganese, such as Mn^{2+}, $Mn^{3+,}$ or Mn^{4+} [5] , p-type change Metal oxides are of great interest because of their participation in a variety of applications, including photovoltaic solar cells, electrochemical energy storage devices, microelectronic devices, and metal-oxide-semiconductor field-effect transistors (p MOSFETs) [6]-[9] , Nickel oxide (NiO) is a crystalline powder, either green or black in color, with density 6.67 g/cm^3, molecular weight 842.87 g/mol, and melting point 1984 C^0 [10] Nickel oxide (NiO) is non-insulating at room temperature and is an antiferromagnetic material with good resistance. It also has a large energy gap estimated at 3.4 - 4 ev and is considered one of the important electrolytic materials after tungsten oxide. It is used in making the electric anode and has several uses due to the high electrolytic efficiency. Nickel oxide has high stability and has positive conductivity [11], A variety of techniques have been used to grow manganese oxide thin films such as chemical bath deposition [12], [13] , dip coat [14] electrochemical deposition [15] , atomic layer deposition [16] , electrostatic spray deposition [17], pulsed laser deposition [18], chemical vapor deposition [19] and SILAR method [20] chemical pyrolysis technique [21], Because it is easy to use, inexpensive, and produces little waste, spray

pyrolysis is a good substitute for conventional methods for creating manganese oxide thin films. It can be applied to a wide surface area and is simple to integrate into an industrial production line. This method works with mass production systems as well [22]

2 EXPERIMENTAL PART

Chemical spray pyrolysis (CSP) method was employed to create thin films of manganese oxide (Mn_3O_4) doped with nickel oxide (NiO). German-made glass plates from Los Las Company were prepared. The plates were cut into (2.5 × 2.5) cm dimensions and rinsed with distilled water for 4 minutes in an ultrasonic device. After that, they were sterilized with acetone for 4 minutes and then again with distilled water. Finally, they were dried with a special fabric to remove the remaining suspended particles. The oxide solution was prepared by mixing manganese chloride ($MnCl_2.4H_2O$) weighing 1.979 g in 100 ml of distilled water. Then, it was placed on a magnetic stirrer for 10 minutes. Then, it was filtered using filter paper. After that, it was deposited using a spray system on the glass plates at a temperature of 350 C^0. The pure oxide films were doped with nickel oxide at ratios of 0%, 1%, 3%, 5% and 7% , 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 produced films' surface morphology was also examined 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

3 RESULT AND DISCUSSION

3.1 Results of Field Emission Scanning Electron Microscopy Tests

Field-emitting scanning electron microscopy (FE SEM) is used to examine the surface topography of all the prepared membranes was studied at a temperature of 350 C^0. This device gives a structural image of the surface with very high accuracy. Figures 1a, 1b, 1d, 1e show FE SEM images and cross sections of the prepared films. It is formed in beautiful shapes, spherical shapes gathered in the form of a flower very similar to a cauliflower flower. It is also irregular in size and distribution and uneven in growth, noting the presence of voids resulting from the occurrence of secondary growth as well as due to crystalline defects. We note that the average crystal size has large differences due to the lack of good homogeneity of the membranes [23], [24] .

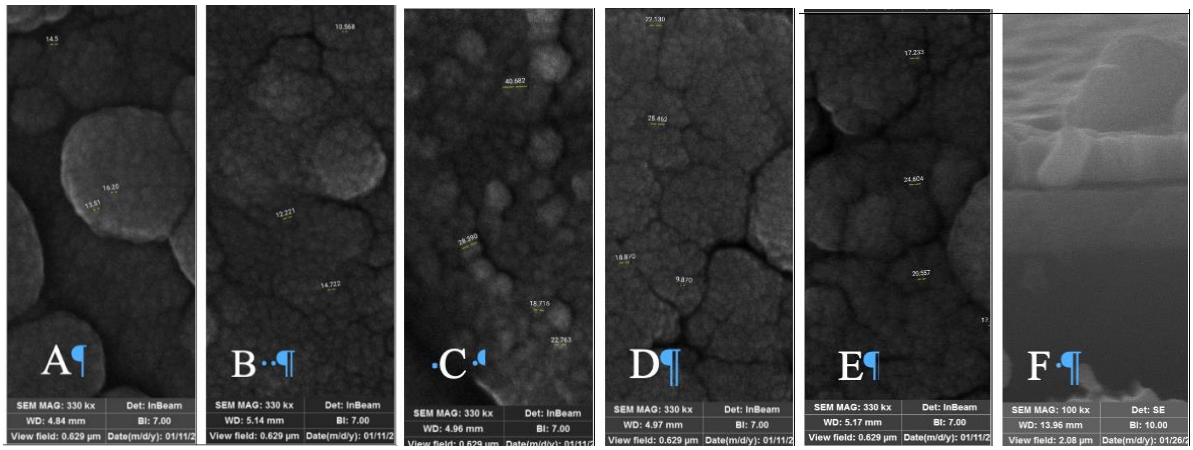

Figure 1: FE-SEM Images of : a) Mn_3O_4: Pure, b) Mn_3O_4: NiO (1%), c) Mn_3O_4: NiO (3%), d) Mn_3O_4: NiO (5%), e) Mn_3O_4: NiO (7%), f) Cross-sectional view showing the film thickness (~327 nm).

We observe that the Mn3O4 membrane with a 7% impurity rate had the biggest particle size, whereas the membrane with a 1% nickel oxide impurity rate had the lowest value. As seen in Figure 1f, the produced film layer has a thickness of roughly 327 nm.

3.2 Results of Energy Dispersive Spectrometer Test

To verify the components of the prepared thin films, we conduct an examination Energy Dispersive Spectrometer (EDS), which is an examination through which the weight percentages and atomic percentages of the elements present in the prepared films that cannot be detected using X-ray technology (XRD). The following Figures 2, 3, 4, 5, 6 are diagrams showing the analysis of EDS and the following Tables 1, 2, 3, 4, 5 show the weight percentages and atomic percentages of the elements present in the prepared films.

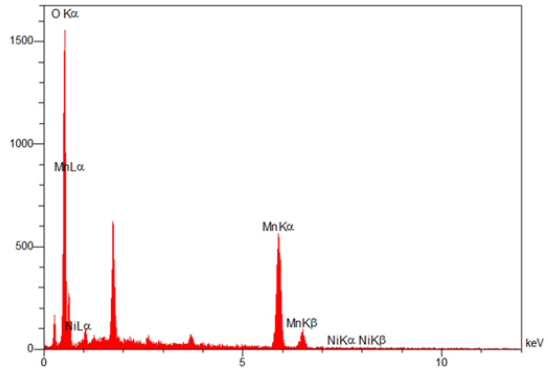

Figure 2: Analysis diagram EDS for a thin Mn_3O_4 film.

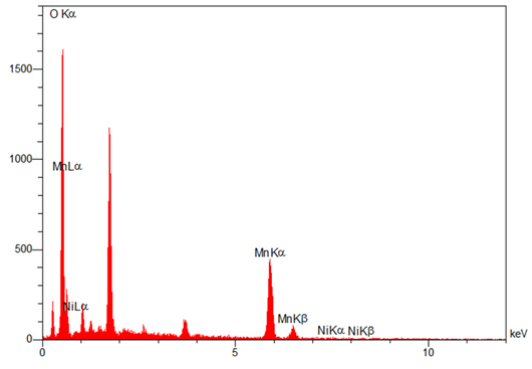

Figure 3: Analysis diagram EDS for a thin Mn_3O_4 film.

Table 1: Weight ratios and atomic ratios of elements in the film Mn_3O_4 for analysis EDS.

Element	Weight (%)	Atomic (%)
O	47.89	75.94
Mn	51.88	23.96
Ni	0.23	0.10

Table 2: Weight ratios and atomic ratios of elements in the film Mn_3O_4 for analysis EDS.

Element	Weight (%)	Atomic (%)
O	54.64	80.54
Mn	45.00	19.32
Ni	0.35	0.14

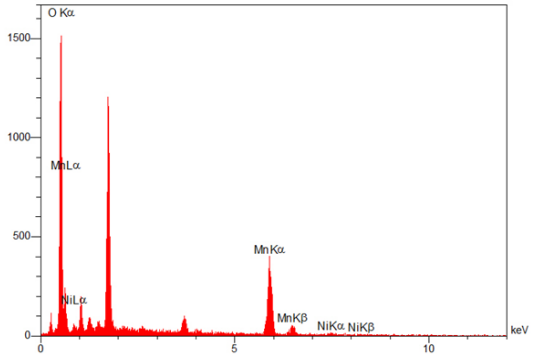

Figure 4: Analysis diagram EDS for a thin Mn_3O_4 film.

Table 3: Weight ratios and atomic ratios of elements in the film Mn_3O_4 for analysis EDS.

Element	Weight (%)	Atomic (%)
O	57.60	82.37
Mn	41.55	17.30
Ni	0.85	0.33

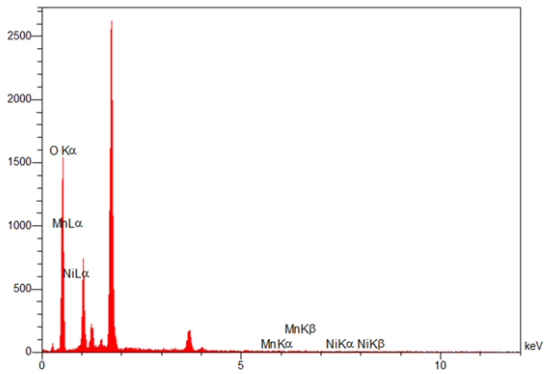

Figure 5: Analysis diagram EDS for a thin Mn_3O_4 film.

Table 4: Weight ratios and atomic ratios of elements in the film Mn_3O_4 for analysis EDS.

Element	Weight (%)	Atomic (%)
O	98.92	99.70
Mn	0.42	0.12
Ni	0.65	0.18

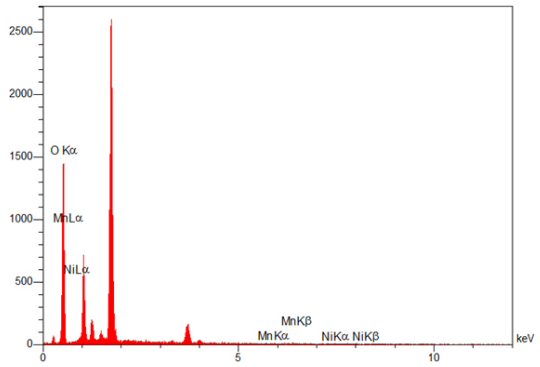

Figure 6: Analysis diagram EDS for a thin Mn3O4 film.

Table 5: Weight ratios and atomic ratios of elements in the film Mn_3O_4 for analysis EDS.

Element	Weight (%)	Atomic (%)
O	98.70	99.63
Mn	0.57	0.17
Ni	0.73	0.20

3.3 Results of Electrical Measurement

The Hall effect was conducted as a measurement to determine the electrical characteristics of Mn_3O_4 films made at 350 C^0 and with impurity rates 0%, 1%, 3%, 5% and 7 % of nickel oxide. Through it the important electrical properties were known, such as the type of charge carriers, their concentration, and the values of the Hall coefficient. It is found that all the prepared Mn_3O_4 due to positive Hall coefficient values, which indicate that holes make up the majority of charge carriers and electrons make up the minority, membranes are of the positive type (P-type) [25] , Table 6 shows the results of the Hall effect , We notice that the values of the effect of the Hall coefficient increase with increasing doping rates, and its highest value is at a doping percentage of 3% of nickel oxide , The results show that the resistivity values of all the prepared films are high, and their highest value occurs at a doping rate of 1% of nickel oxide. The reason for the high resistivity values is the crystalline defects resulting from Ni ions, as they restrict the movement of electrons and increase their resistance [26]. All produced membranes had low conductivity values , as we note that they increased after the doping process with nickel oxide, and their highest value was at the doping rate of 7% of nickel oxid ,The reason for the increase in conductivity is the replacement of Mn_3O_4 with NiO ions, which gives the electrons increased freedom and leads to an increase in electrical conductivity [27], [28]. The mobility increases with increasing doping rates, and its highest value was at a doping percentage of 7% of nickel oxide, Figures 7, 8, 9 shows the values of resistivity , Hall coefficient , and charge carrier concentration as a function of doping ratios, respectively, for all prepared films.

Table 6: Hall effect measurements for the prepared thin films.

Sample	Concentration $(cm)^{-3}$	Hall Coefficient RH (m^2/C)	Conductivity $(\Omega.cm)^{-1}$	Resistivity $(\Omega.cm)$	Mobility $(cm^2/v.s)$
Pure	2.025×10^{11}	3.082×10^{7}	0.772×10^{-5}	12.98×10^{4}	2.374×10^{2}
Mn_3O_4: NiO (1%)	2.748×10^{11}	2.271×10^{7}	0.523×10^{-5}	19.15×10^{4}	1.186×10^{2}
Mn_3O_4: NiO (3%)	10.52×10^{11}	0.5934×10^{7}	2.017×10^{-5}	4.829×10^{4}	1.229×10^{2}
Mn_3O_4:NiO (5%)	1.912×10^{11}	3.265×10^{7}	1.247×10^{-5}	8.016×10^{4}	4.073×10^{2}
Mn_3O_4: NiO (7%)	2.014×10^{11}	3.100×10^{7}	1.614×10^{-5}	6.198×10^{4}	5.002×10^{2}

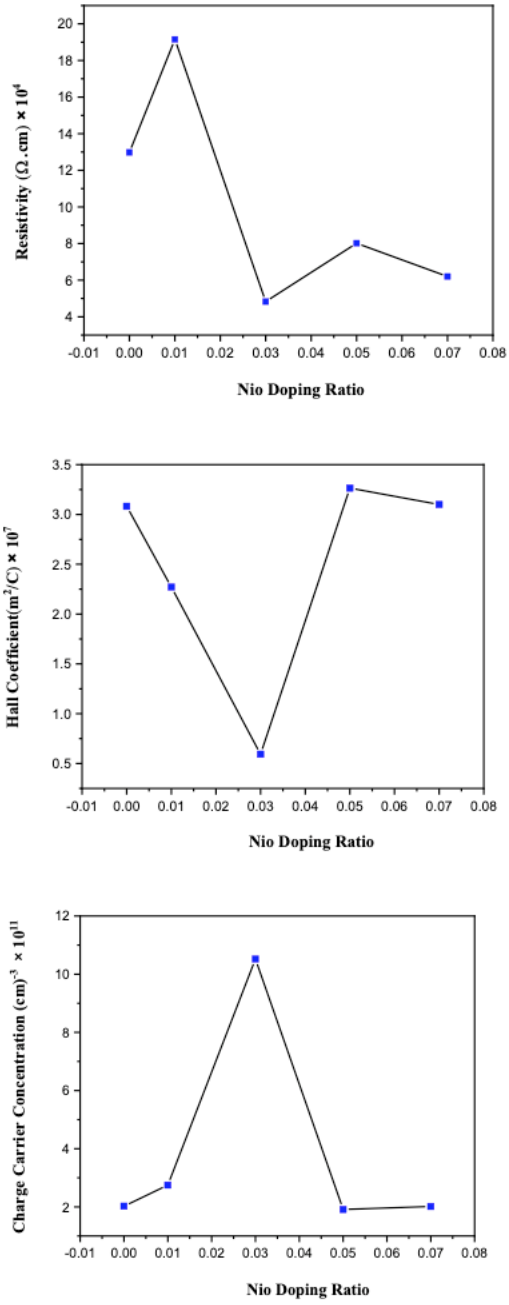

Figure 9: Concentration of charge carriers as a function of doping ratios for the prepared films.

4 CONCLUSIONS

This study demonstrates that NiO doping has a significant impact on the morphological and electrical properties of Mn_3O_4 nanostructured thin films. SEM analysis revealed a cauliflower-like, spherical morphology and pronounced size irregularity, attributed to crystalline defects—the largest particle size was observed at 7% NiO content. EDS confirmed the presence of Mn, O, and Ni, with manganese concentration declining and nickel peaking at intermediate doping levels.

Electrical measurements showed all films exhibit p-type conductivity. The Hall coefficient reached its maximum at 3% NiO, while resistivity peaked at 1% doping and conductivity and carrier mobility were highest at 7% NiO. These trends indicate that controlled NiO doping efficiently tailors film properties, with optimal electrical characteristics achieved at specific doping ratios. Overall, the findings support the use of NiO doping to optimize Mn_3O_4 thin films for applications in electronic and energy devices.

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