Study of the Effect of Manganese on The Structural and Optical Properties of Sno2 Membranes

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KEYWORDS
XRD ,SEM, Energy gap, Absorption, permeability, sensitivity

ABSTRACT
The effect of manganese addition on precipitated tin dioxide on quartz was studied using the pulsed laser method if the X-ray diffraction results showed that the pure tin oxide membrane has a polycrystalline structure and a quaternary phase, with growth in the crystalline directions (110), (101), (200), and (211) and the predominant ones were (101). Using a high-benefit electron scanning microscope (FE-SEM), the results showed that the addition of manganese smearing in small proportions significantly affected the surface nature and grain size, as the surface uniformity and grain size increased with increasing the percentage of distortion. Through optical examinations through the permeability spectrum of thin films of pure and tinged tin oxide, a gradual increase in permeability with an increase in the concentration of impurities, reaching high values ranging between 80-90%. As for the energy gap, the energy gap for manganese-inlaid membranes has been increased from 3.33 eV for the pure membrane to 3.57 eV. The sensing properties of these membranes were studied as a function of time at temperatures between 50-200 °C .

1. Introduction

Thin films are materials with thicknesses ranging from a few nanometers to several micrometers, and they have unique properties due to this tiny thickness. Due to the thinness of these membranes, the ratio of surface area to volume is enormous compared to traditional thick materials. This gives it outstanding physical and chemical properties in the electrical, optical, thermal and other fields. There are several ways to manufacture these thin films.[1,2] The most prominent of these are: evaporation deposition, where the material is deposited on another surface using heat or plasma evaporation. There is also the method of chemical deposition from vapor, which relies on chemical reactions in the gas to precipitate the substance on the surface. There are also methods of acidification, centrifugation, loading and electrode position[3,4].

The main applications of thin films include electronics fields such as chips, screens, solar cells and sensors. They are also used in the field of energy in solar cells, batteries and fuel membranes. In the medical field, it is used in biomedical membranes, filtration membranes and neurostimulation. Environmental applications such as purification and filtration membranes and protective coating membranes. It is also used in precision optical instruments such as mirrors and lenses. Thin films therefore have enormous potential and diverse applications in various biological and industrial fields, thanks to their unique properties resulting from their thin thickness[5,6].

Tin oxide (SnO2) membranes are a type of thin film that has unique properties and diverse applications. SnO2 is an inorganic compound that has a certain crystal structure that gives it important semiconductor properties. Here are some of the main characteristics of SnO2 membranes[7,8]:

1. Optical transparency: SnO2 membranes are transparent in the visible range of the light spectrum, making them suitable for transparent optical and electronic applications.

2. Electrical conductivity: SnO2 is a semiconductor with a large power gap, which makes it a good conductor of electricity when grafted with suitable impurities.

3. Thermal and chemical stability: SnO2 membranes have good thermal and chemical stability, making them suitable for applications in extreme conditions.

4. Sensitivity to gases: SnO2 has gas-sensitive properties, making it suitable for gas sensing

applications.t.

2. Methodology

Preparation of tablets Sno2 tarted Mn

The main material that was used is Sno2 tin dioxide powder with high purity of (99.99%) and produced from the American company (Product of USA), and manganese powder was used Mn from a Swiss company with a purity of 99%. Initially, the samples were weighed with a weight of (3gm), one of which is pure tin dioxide, in addition to five samples tinged with manganese with distortion rates of (1,2,4,6,8)% using a sensitive electronic balance with four decimal places after the sorter produced by the American company Metller A.K-160. Where the mixture was grinded using ceramic mortar for a period of (30) min, then the mixed powders were pressed with a compression force (4) Ton in a special mold made of alloy steel material with the inner diameter of the mold (1.2 cm) and a thickness of (0.5 cm) and for a period of 10min) .

Technical using pulse laser deposition and principles of thin films :

We place pure SnO2 tablets or tinged with the element Mn in proportions of (1,2,4,6,8)% inside the sedimentation chamber and be directly below the sedimentation bases so that the atoms and molecules of the target material on which the laser beam fell evaporate in the form of plasma that can be seen with the naked eye, and then the bases are deposited directly, and that the process of growth and sedimentation of thin films can be summarized in the following points: - The interaction between the falling laser beam with the atoms of pure Sno2 material or tinged with proportions of Mn. The plasma state is formed inside the sedimentation chamber facing upward towards the sedimentation bases fixed above the disk (target) by a distance of mm(20). Deposition of the target material on the slides. After the nozzle. The laser beam makes an angle of˚45 on the surface of the target material.

The measurement :

In this research, measurements were made on the thin films deposited from pure Sno2 materials and tinged with proportions of Mn after annealing using pulsed laser deposition technique (PLD) on quartz slices, and we measured the optical, structural and electrical properties of thin films and then used as a gas sensor (NF3) and physical calculations were performed on them.

Optical properties measurement

We made optical measurements of the membranes of SnO2 and tinged with different percentages of Mn, which were deposited on slices of quartz at room temperature using pulsed laser deposition technique (PLD), and we performed visual examinations on quartz strips that were plasticized at a temperature of c(˚ 800), through the permeability spectrum using the spectrometer of the type (UV/visible sp - 8001 spectrophotometer) of German origin, which has a spectral range of nm (1100-200) so that this spectrometer contains two optical candles of toxten and deuterium with lengths Wave nm(190-390) (390-1100) respectively, where we zero the device by placing a slice of quartz - according to the sample used - pure undeposited on it, and then put the chip on which the membrane is deposited to record the reading spectrum of absorption of the membrane after subtracting the reading of the absorption spectrum of the pure quartz slice that is not deposited on it, and we recorded all readings at room temperature, where we recorded optical readings represented by measuring transmition T (Transmition) and absorbability A (Absorption) as functions and parameters of wavelength User.

2X-ray diffraction instruments (XRD)

X-ray generator device was used to study the crystal structure of pure SnO2 films infested with thin Mn prepared with pulse laser deposition technique for plasticized samples at a temperature of (800°C) for quartz bases. We studied the membranes prepared on quartz slices through the pattern of X-ray diffraction that shows peaks due to Braque reflections and parallel crystalline surfaces, and this indicates the presence of a number of values in the graph that we obtained from X-rays on the crystalline nature of the samples examined, as the waves reflected from the crystalline surfaces are similar waves as they emit from the same source and produce constructive interference (subject to Braggs' law) (Braggs Law).

Scanning Elecronic Microscope SEM

In order to identify the nature and morphology of the surface of the prepared membranes more accurately and very correctly calculations, through which it is possible to know the shape and density of surface structures and reveal the sites of defects in the crystal structure through a high-resolution, magnified and detailed image in two dimensions and in black and white. The Dutch-origin MIRA3-TESCAN scanning electron microscope was used. By shining a beam of electrons by the electronic cannon scanner on the surfaces of the membranes to be studied, and through the movement of electrons on the surface of the sample back and forth, the surface of the membrane is scanned to know its topographic details and to know the type of membranes formed:

3. Results and discussion

X – Ray Diffraction Results

Figure (1) shows the results of X-ray diffraction of pure SNO2 tinged with manganese Mn at the beginning of the shape Pure material of tin oxide that this membrane has a polycrystalline structure and that this examination shows that the thin film of the tetragonal phase The figure shows the growth of four crystalline directions (110), (101), (200), (211) and the dominant ones were (101) and this is consistent [9] and that these results were matched with the international label for the examination of materials ASTM numbered (00-100-0062).

When adding impurities with magnesia Mn and through the diagram the appearance of the peak of the element magnese at the angle 44.43° and this is identical with the international card with the number (00-151-2520) in addition to the tops of SNO2 and that Figure (1) shows an improvement in the crystal structure when adding, the top of the manganese element increases in intensity and is accompanied by a decrease in the peaks of the intensity of tin (II) oxide, and this indicates an increase in crystallization and homogeneity between the granules of the material, meaning that this addition led to improving the crystal structure and increasing the regularity of the material due to filling the voids In addition, the impurity worked to form special atomic levels within the crystal lattice of the tainted material, and that the crystal size of the prepared membranes decreases when the addition of manganese increases[10].

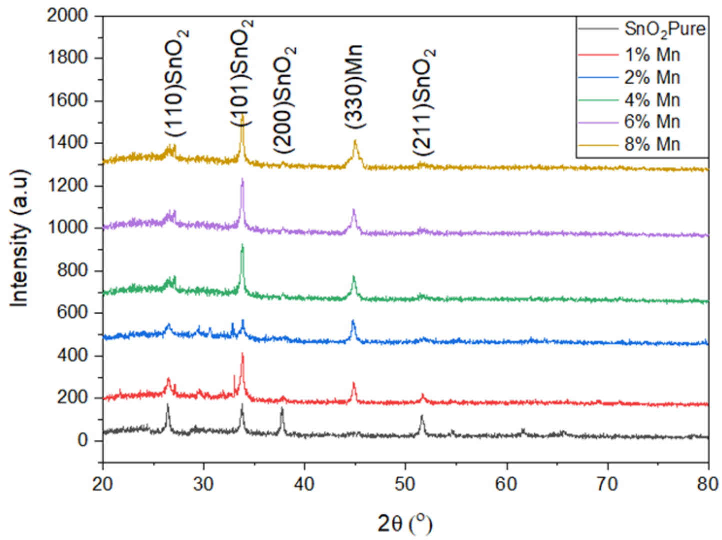

Figure (1) X-ray diffraction of pure manganese-inlaid SnO2 membranes in different proportions

Field emission Scanning Electron Microscope Results

All samples of pure and manganese-tinged tin oxide films were examined using scanning electron microscopy (FE-SEM) technology for the purpose of identifying the nature of the membrane surfaces and observing the change of granular size with changing the preparation conditions, as we can observe through the tests and images shown in the SEM shapes that the addition of impurities in certain small proportions had a great impact on the formation of the shape of the surface structure features of the prepared membranes. And that all prepared membranes have granules of almost uniform distribution, and with increasing the percentage of distortion, the surface of the pure SNO2 membrane becomes less homogeneous and regular, so the crystal structure begins to disintegrate and change according to the compatibility of the quality of the prepared membrane and this behavior is compatible with the researcher [11].

The increase in the percentage of manganese distortion led to an increase and then a decrease in the granular size as a result of the effect of the impurity atoms involved in the composition of the material, and this corresponds to the results of X-ray diffraction tests (XRD). The addition of manganese increased the granular size and increased the uniformity of the surface and there appeared there are surface cracks and few agglomerates and that the granular distribution of the average diameters was uniform as in figures.(2)

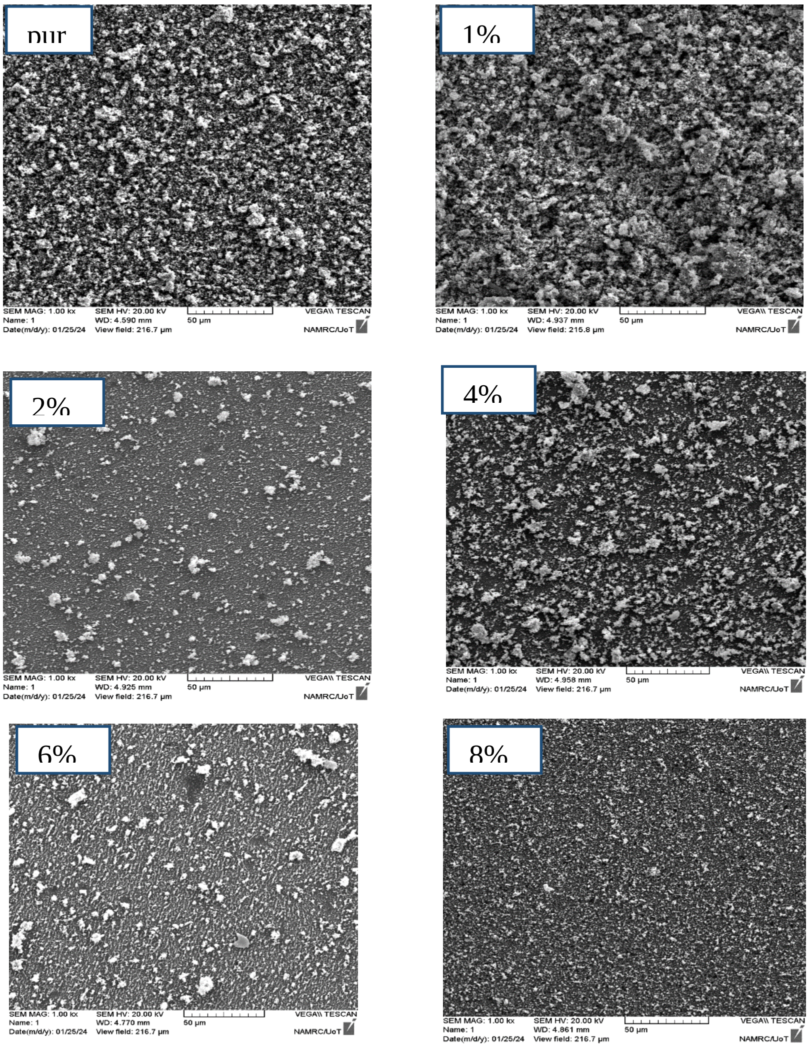

Figure (2) shows the FESEM output of the smelted pure SNO2 membranes

Transmittance Spectrum

Transmittance measurements were carried out in the range of wavelengths 300-1100nm for all pure and tinged membranes after being deposited on glass floors and the transmittance spectrum is opposite by its behavior of the absorption spectrum, tin oxide SnO_2 is one of the types of semiconductor materials with high permeability in the visible region, these results showed that there is an increase in the value of permeability whenever the percentage of impurities increases as in Figure (3), as tin oxide membranes have the highest permeability by % (80-90) at the degree of Room temperature within the visible spectrum region with low permeability in the ultraviolet region, and shows the permeability spectrum as a function of the wavelength of pure tin oxide films tinged with manganese at the distortion ratios.(1,2,4,6,8) %

In general, the transmittance curve of samples usually shows similar optical behavior, as it shows a gradual semi-stable increase starting from the wavelength of approximately 300 nm, and this behavior is identical to the behavior of the transmittance curve in the transparent conductivity oxides group: TCO, where the transmittance increases rapidly at the cutting edge area, which confirms that the energy gap of the membranes is of the direct type as well Figure (3) shows a gradual increase in permeability with an increase in the distortion ratios taken, and the increase in the transmittance spectrum can be attributed The membrane is characterized by a decrease in the absorption of illumination by the localized levels formed due to impurities within the energy gap present, and because the transmittance spectrum depends on the chemical composition of the material, the thickness of the membrane, the topography of the surface and its reflectivity, and it can be concluded from the transmittance spectrum also that these prepared membranes are considered a window to the visible and infrared regions, which we will benefit from when manufacturing the photodetector[12].

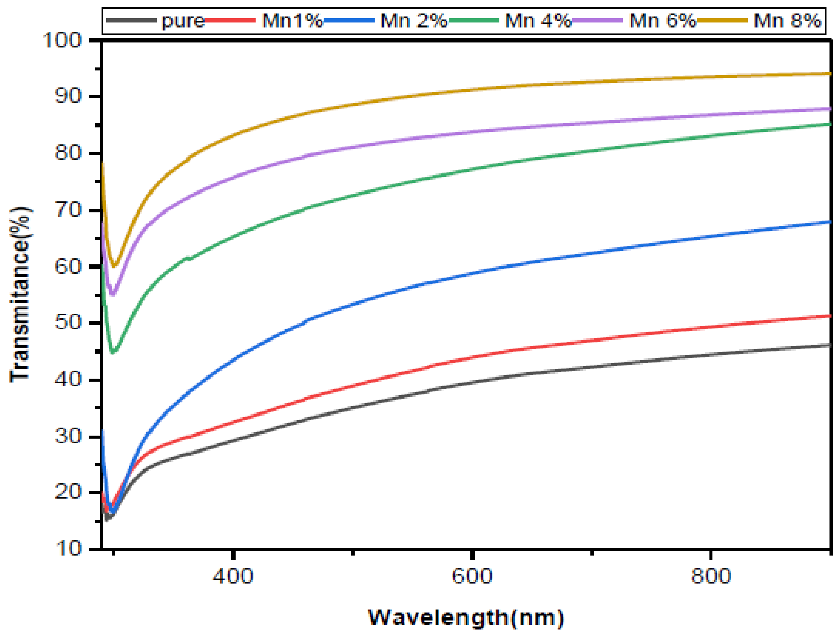

Figure (3) represents the permeability spectrum of pure and tinged membranes

Absorptance Spectrum

Absorbance generally depends on the energy of photons incident on the semiconductor material, on the type of material, the nature of its crystal structure, on the surface roughness and on the locations of impurities in the material. The core absorption edge represents the lowest difference in energy between the highest point in the valence beam and the lowest point in the conduction beam and also represents the boundary between the high absorption area of light and the transparent area of pure and tinged samples and on this basis we find from Figure (4) that there is a slight displacement in the curves at the edge of the basic absorption towards the shorter wavelengths, it is expected for this displacement in the curves at the edge of absorption that the increase in distortion will lead to a magnification of the energy gap present, and if This change in absorption edge values is important in window layer coating applications that prevent unwanted absorption in the Luminous Spectra range. This is because the distortion has increased the Sniper positional levels near the delivery package[13].

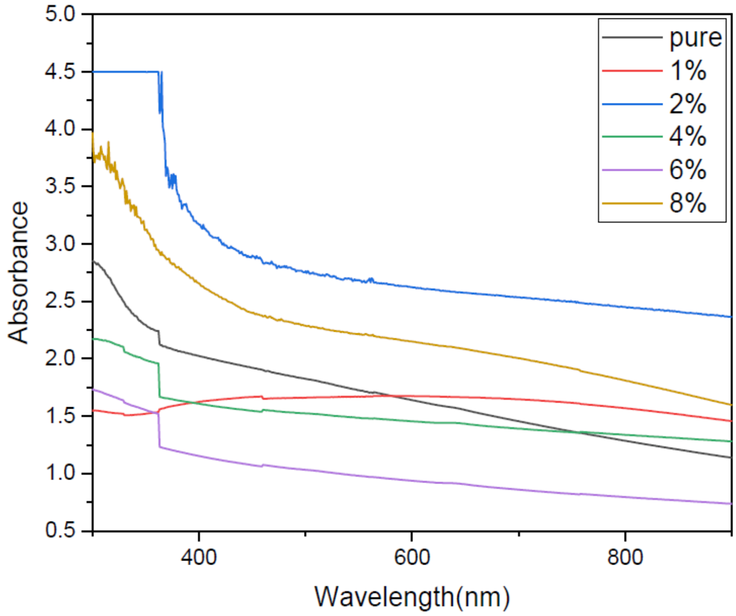

Figure (4) The absorbency spectrum is a function of the wavelength of pure and smeared samples

The Optical Energy Gap

Figure (5) shows the energy gap of the prepared membranes as the optical energy gap of all pure and tinged SNO2 membranes is calculated by drawing a relationship of change (αhv)2 with the energy of the incident photon (hv) as shown in Figure (5), as this figure (12-4) shows that the change is linear in a certain range of photon energies (the range of the visible region). The energy gap value of the pure SnO2 membrane was equal to (3.33 eV) which corresponds to a high absorption coefficient of (8X10-4 cm-1), which confirms that the nature of the transitions of these membranes has a direct transmission allowed and that the energy gap is a direct energy gap, and so on for all prepared membranes.

As for the effect of distortion on the energy gap, the increase in morphography led to a clear increase in the energy gap value from (3.33 eV) for the pure membrane to (3.57 eV) as shown in Table (1) for the inlaid membrane [14], and thus the absorption of photons with lower energies will be difficult.

Table (5) shows the energy gap values of pure and smeared SNO2 membranes

Sample	**E_g(eV)**
pure	3.33
Mn 1%	3.38
Mn 2%	3.42
4% Mn	3.48
6% Mn	3.52
8% Mn	3.57

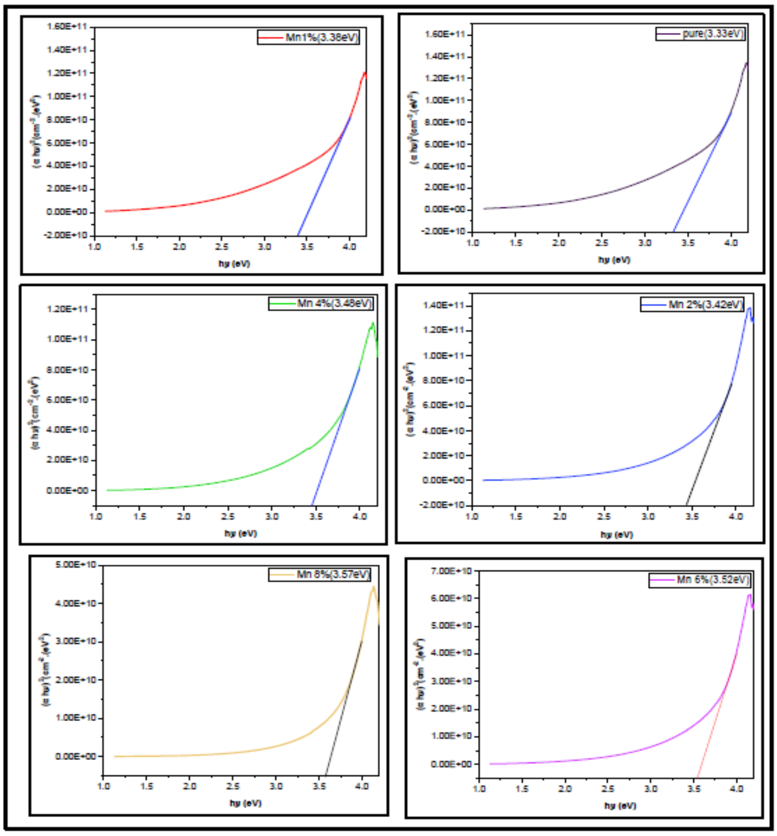

Figure (5) Optical energy gap of permissible direct transmission of pure and smeared (Mn) SNO2 membranes with different distortion ratios

4. Conclusion and future scope

The pure tin oxide membrane has a polycrystalline structure and a quaternary phase, with major growth in the crystalline directions (110), (101), (200), and (211), and the direction (101) predominant. The addition of manganese in small proportions to the tin oxide membrane led to improved surface homogeneity and an increase in grain size. The increased concentration of impurities (manganese) in the tin oxide membrane led to a gradual increase in the optical transmittance of the membrane, reaching high values between 80-90%. The addition of manganese to the tin oxide membrane increased the energy gap of the membrane from (3.33 to 3.57) eV. The pure membrane showed sensing sensitivity from 13.8% at 50°C to 32% at 200°C.

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