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Effects of Mn concentration on the performance of ZnO thin film humidity sensor

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Abstract

ZnO is considered one of the most promising semiconductors for use as a sensing material due to its superior electrical properties, wide band gap, and high surface-to-volume ratio. Due to their enhanced sensitivity, stability, and cost effectiveness, recently there has been much interest in using ZnO thin films as humidity sensors. In this work, successful growth of Mn-doped ZnO thin films on FTO glass substrates via the spin coating process was demonstrated. Effects of different doping percentages of manganese (0%, 2%, 4%, 6%, and 8%) on properties of ZnO thin films have been investigated. A precursor solution was prepared using zinc acetate and manganese acetate, ensuring uniform mixing for controlled doping. The prepared films were deposited using a repeated spin coating process followed by annealing at 400 °C to improve crystallinity and film quality. Morphology, optical and electrical properties of the films were studied, along with the sensing properties at various levels of relative humidity. It was found that the electrical resistances of all the films decreased with increased humidity due to adsorption of water molecules on the surface resulting in better charge transport in the film. Among all the films investigated, 4% Mn-doped film showed superior performance as it had maximum sensitivity, response time, recovery time, and good electrical conductivity compared to other films. From the I-V measurement, it was found that the 4% Mn-doped ZnO film had higher current response than the other films. Optical studies show that the optimized film had a band gap value of 3.22 eV. In general, it can be concluded that 4% Mn-doped ZnO thin films fabricated using the spin-coating technique are very promising candidates for humidity sensing applications.

Keywords: Humidity sensor, spin coating, sensitivity, response time, recovery time

Introduction

Humidity is one of the most important environmental parameters, which plays an important role in many physical, chemical, and biological processes in many fields such as agriculture, healthcare, food storage, and industrial manufacturing. Accurate humidity monitoring is critical for maintaining product quality, ensuring process efficiency, and preventing equipment damage. Excessive humidity can cause corrosion of metal components, damage of electronic devices, and promotion of microbial growth, whereas low humidity can cause material drying and malfunction of sensitive equipment [1, 2]. Humidity sensors have become an important tool for environmental monitoring and control. They are used in agriculture crop optimization, healthcare equipment, pharmaceutical storage, and industrial manufacturing processes [2, 3].

Various materials have been investigated for humidity sensing applications, including polymers, ceramics and semiconductor metal oxides. Among them, metal oxide semiconductors are preferred due to their superior sensitivity, chemical stability, low cost of fabrication and compatibility with miniaturization technologies. The electrical properties of water molecules are

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significantly affected on the surface of materials such as Zinc oxide (ZnO), tin oxide (SnO_2) and titanium dioxide (TiO_2) which makes them ideal for accurate humidity sensing [3]. ZnO is a popular n-type semiconductor with a large band gap (~ 3.3 eV), high electron mobility and excellent chemical and thermal stability. Its inherent defects such as oxygen vacancies and zinc interstitials enhance the adsorption of water molecule on the surface of the material [4]. The interaction of water molecules with ZnO causes measurable changes in electrical conductivity and thus ZnO is suitable for humidity sensing applications. ZnO is non-toxic, environment friendly and cheap with compatibility of simple techniques of fabrication such as spin coating [5].

However, pure ZnO has some limitations such as moderate sensitivity, relatively slow response and recovery time, and limited electrical conductivity. These limitations demand modification strategies such as doping to enhance the sensing properties of ZnO [6]. Doping is the deliberate addition of impurity atoms to a semiconductor lattice in order to modify and improve its characteristics. Doping enhances electrical conductivity by increasing the concentration of charge carriers and generating defect sites and oxygen vacancies, which act as active adsorption centers for target molecules [7, 8]. Transition metal doping with elements such as manganese (Mn), Cobalt (Co) and Nickel (Ni) alters the electronic structure, increases the electrical conductivity and boosts the charge carrier mobility, creating more active sites for water molecule adsorption [9].

Manganese (Mn) is a good dopant for ZnO because its ionic radius is close to that of zinc ions (Zn^{2+}), so it can be substituted easily without much distortion in the structure. Mn doping leads to the increase of the concentration of oxygen vacancies and the formation of new defect sites that are beneficial for the adsorption of water molecules on the surface of ZnO. The Mn-doped ZnO thin films have better electrical conductivity and humidity sensing performance than the pure ZnO due to the increase in surface roughness and the formation of more active sites [10]. The humidity sensing performance is greatly affected by the concentration of the Mn dopant. The optimal concentration enhances the number of active surface sites and the mobility of charge carriers. However, high doping levels result in the formation of defects and secondary phases that reduce the electrical conductivity and hinder charge transfer [10]. The importance of optimizing the dopant concentrations for the sensing performance has been pointed out recently [11, 12].

ZnO is a well-studied material for humidity sensing. Farahani et al. showed that electrical resistance of ZnO changed dramatically with relative humidity [10]. Chen and Lu reported that the sensitivity was improved due to the high surface-to-volume ratio of ZnO nanostructures [3]. Numerous researchers have examined the sensing capabilities of ZnO doped with transition metals, and Mn-doped ZnO has drawn a lot of interest because of the appropriate ionic radius of Mn ions. Due to an increase in oxygen vacancies and defect sites, Mn-doped ZnO thin films were shown to be more sensitive than pure ZnO [1]. Similarly, Zhang et al. [12] reported that moderate Mn concentrations improved the charge carrier transport and adsorption behavior considerably. The humidity sensing mechanism is related to the chemisorption of water molecules at low humidity levels, forming hydroxyl groups, and physisorption and multilayer formation at high humidity levels, enabling proton transport through the Grotthuss mechanism, and resulting in enhanced conductivity [13, 14]. Many studies have been done on ZnO based humidity sensors but the changes in fabrication processes, dopant concentrations and sensing

conditions affect the performance of the sensors. Few studies have been done on spin-coated Mn-doped ZnO thin films under low-cost laboratory conditions.

The present study focuses on preparing Mn-doped ZnO thin films on FTO-coated glass substrates through the sol-gel spin coating technique. It investigates how the structural, optical, electrical, and humidity sensing characteristics are affected by different Mn doping concentrations (0%, 2%, 4%, 6%, and 8%). It also studies the humidity sensing performance in terms of sensitivity, response time, recovery time and electrical conductivity to find the optimal Mn doping concentration for enhanced humidity sensing performance.

Materials and Methodology

Materials

Analytical grade chemicals were used as received. The Zn precursor was zinc acetate dihydrate ($Zn(CH_3COO)_2 \bullet 2H_2O$, 99.9% purity) and the dopant source was manganese acetate tetrahydrate ($Mn(CH_3COO)_2 \bullet 4H_2O$, 99.9% purity). Ethanol (99.9% purity) was used as the solvent and acetylacetone was used as the stabilizer to improve the homogeneity of the solution.

Preparing the Substrate

FTO-coated glass substrates were cut into 2 cm x 1 cm pieces. The substrates were cleaned in an ultrasonic bath sequentially with acetone, ethanol and distilled water for 10 min each time. The middle conducting region was selectively removed by zinc powder and HCl to define the sensing area, which was checked by a multimeter. Substrates were re-cleaned and dried after etching.

Preparation of Precursor Solution

Zinc acetate dihydrate (0.1 M) was dissolved in ethanol and then manganese acetate tetrahydrate was added according to the required doping concentrations (0%, 2%, 4%, 6% and 8% according to zinc content). The solution was stirred at room temperature for 30 min to ensure complete dissolution. Acetylacetone (stabilizer) was added dropwise to control the hydrolysis and prevent precipitation. The solution was stirred until a clear homogeneous mixture was obtained and stored in a closed container.

Thin-film Deposition

Mn-doped ZnO thin films were deposited by a two-step spin coating process. About 0.1 mL of precursor solution was dropped on the substrate and spin coated at 500 rpm for 5 seconds (spreading step) and then at 2000 rpm for 30 seconds (uniform film formation). After each coating cycle, samples were dried on a hot plate at 100 °C for 10 minutes. The procedure was repeated for 5 cycles to obtain the desired film thickness.

Annealing

The coated films were annealed at 400 °C for 1.5 h in the box furnace with the heating rate of 5 °C/min. This annealing step improved crystallinity, removed organic residues and improved film stability and adhesion.

Creation of humidity environment and humidity sensing measurements

Saturated salt solutions were used to provide controlled relative humidity environments. Solution of magnesium chloride ($MgCl_2$) was used for ~33% RH, sodium chloride (NaCl) for 75% RH and potassium chloride (KCl) for 85% RH. The fabricated samples were placed in sealed containers near the saturated salt solution to expose them to the humid environment without direct contact with the liquid.

Measuring Resistance

The electrical resistance of Mn-doped ZnO thin films was measured by using a digital multimeter under different RH conditions. Electrical contacts were made by connecting conducting wires to the exposed FTO regions on either side of the deposited film using crocodile clips. The resistance values were measured after the time taken for stabilization at each humidity level.

Response and Recovery Time

Response time was defined as the time taken for the sensor to reach 90% of the total resistance change when exposed to a higher humidity environment. The recovery time was defined as the time needed for the sensor to achieve 90% of its initial resistance value when taken out of the humid atmosphere. These measurements were performed by continuously monitoring the resistance change by switching at different humidity levels.

Current-Voltage (I-V) Measurements

I-V measurements were performed by applying a DC voltage across the Mn-doped ZnO thin film and measuring the current using a digital multimeter. Measurements were performed under high relative humidity conditions (~85% RH) to enhance charge transport and to enable accurate current measurement.

Computation of Sensitivity

Sensitivity (S) was calculated from the resistance values measured in different RH conditions:

$$S = \frac{R_{low\ RH} - R_{high\ RH}}{R_{low\ RH}}$$

where R_{low} and R_{high} represent the resistance values at low and high relative humidity levels, respectively.

The reduction of resistance at high humidity is due to the adsorption of water molecules which improves ionic conduction.

UV-Vis Spectroscopy

The prepared thin films were investigated by UV-Vis spectroscopy for their optical properties. The absorbance spectra of all samples were recorded in the wavelength range of 300-700 nm using spectrophotometer with bare FTO/glass substrate as the reference.

FTIR Spectrum

Fourier Transform Infrared (FTIR) spectroscopy was used to confirm Zn-O bond formation and identify functional groups. Spectra were taken in the 400-4000 cm^{-1} range at room temperature.

Results and Discussion

Sensitivity Analysis

The sensitivity of the Mn-doped ZnO thin films was calculated from the low and high humidity resistance change. Figure 1 shows the change in sensitivity with Mn doping concentration.

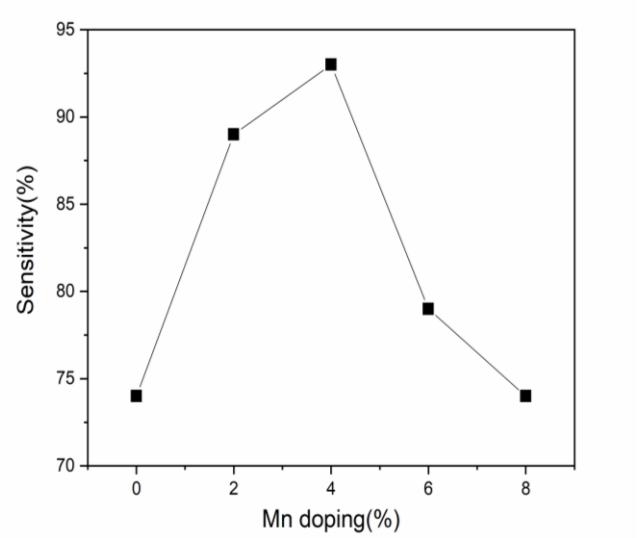


Figure 1: Variation of sensitivity of Mn-doped ZnO thin films.

The undoped ZnO thin film exhibited sensitivity of ~73%, which is relatively low compared to the doped samples due to limited active adsorption sites on the surface. The sensing performance increased considerably by the addition of Mn to the ZnO lattice. This improvement can be ascribed to the increase of oxygen vacancies and defect sites induced by Mn doping. These defects could serve as active centers for adsorption of water molecules and therefore improve the interaction between sensing material and surrounding humid environment [1, 5].

Among all the investigated samples, the 4% Mn-doped ZnO thin film exhibited the highest sensitivity of ~93%. This shows that 4% Mn is the best concentration for humidity sensing applications. The trade-off between defect generation and electrical conductivity at this doping level is favorable for efficient adsorption and charge transport. The larger number of adsorbed water molecules facilitates the proton conduction on the film surface resulting in a large reduction of the resistance under humid conditions [3].

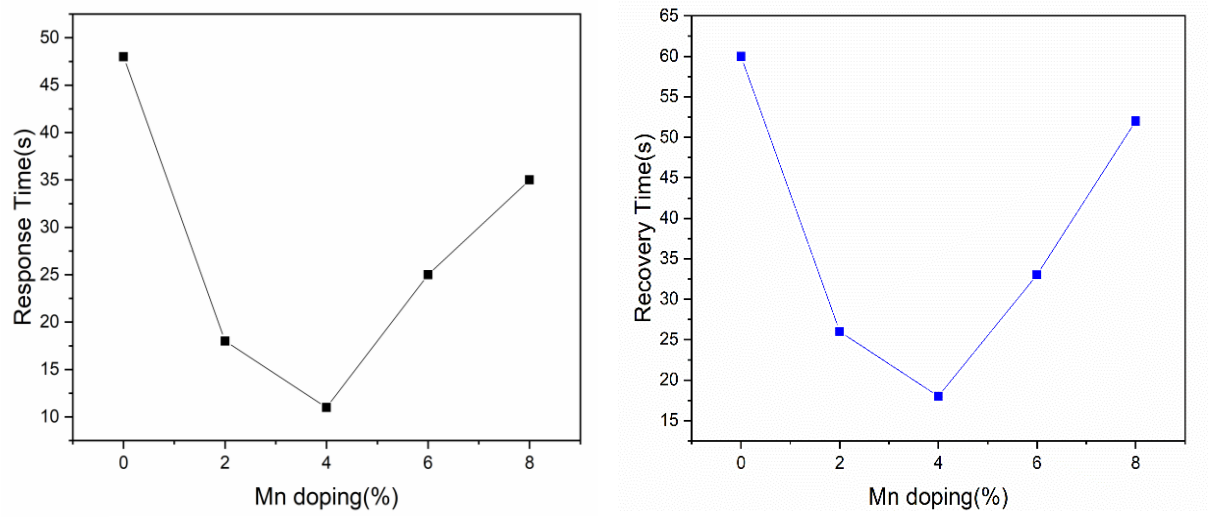
The 2% Mn-doped sample sensitivity was ~89% and the 6% Mn-doped and 8% Mn-doped samples were ~78% and ~73% respectively. The reduced sensitivity at higher Mn concentrations (6% and 8%) can be attributed to the over-insertion of Mn which leads to defect clustering and structural distortion in the ZnO lattice. These effects can decrease the mobility of charge carriers and limit the effective adsorption of water molecules on the surface of the film. Hence, the sensing response is less pronounced than for the optimally doped sample [1, 4].

Response and Recovery Time

The response and recovery times are important parameters that determine the practical applicability of humidity sensors. Response time is the time taken by the sensor to reach a value

close to 90% of the final resistance when exposed to humidity. Recovery time is the time taken to return to its original state after removing humidity [15].

As shown figure 2, the results reveal that the response and recovery times decreased significantly with the Mn doping up to 4%. The ZnO thin film doped with 4% Mn showed the shortest response time (~10 s) and recovery time (~15 s), implying fast adsorption and desorption of water molecules. This behavior is attributed to the increase in the number of active adsorption sites and the improvement of charge transport pathways induced by Mn doping [16].



(a) (b)

Figure 2: Response time (a) and recovery time (b) of Mn-doped ZnO thin films.

The fast response of the 4% sample demonstrates an effective interaction of water molecules with the sensor surface. A short recovery time also indicates the ability to quickly desorb water molecules when the humidity drops. These features are highly desirable for real time monitoring applications where rapid detection and recovery is required.
At higher Mn concentration, the response and recovery times were increased. This can be related to excessive defect formation and decreased carrier mobility which can slow down adsorption and desorption processes. Thus the 4% Mn-doped ZnO thin film exhibited the best dynamic sensing performance among the studied samples.

Current–Voltage (I–V) characteristics

The electrical behavior and charge transport properties of the fabricated Mn-doped ZnO thin films were investigated by measuring their current–voltage (I–V) characteristics under high humidity conditions. The I-V characteristics are presented in figure 3.

For all doping concentrations, the measured I-V curves exhibited an almost linear relationship between the current and the applied voltage. The linear behavior implies an ohmic conduction, meaning that the electrical contacts between the FTO electrodes and the sensing layer were stable and no significant barrier existed at the interface [5].

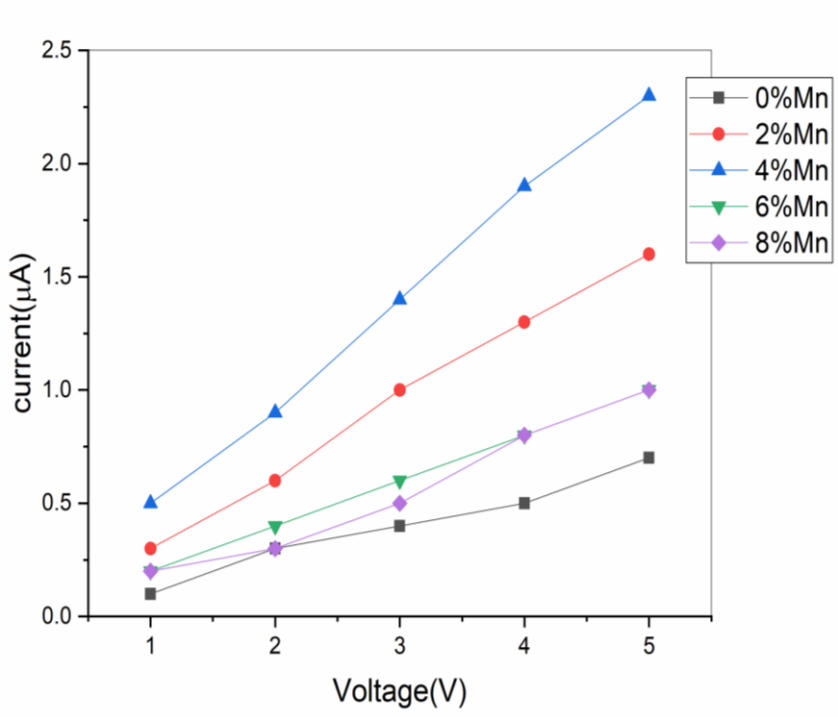


Figure 3: I-V characteristics of Mn-doped ZnO thin films at 85 % RH

The undoped ZnO sample presented relatively low current values attributed to its limited charge carrier concentration and fewer active adsorption sites. The addition of Mn resulted in a significant increase in current, indicating improved conductivity. The incorporation of Mn ions into the ZnO lattice generated more defect states and oxygen vacancies, which increased the generation and transport of charge carriers. These defects also acted as adsorption sites for water molecules, further enhancing the conductivity.

Among all the samples studied, the 4% Mn-doped ZnO thin film registered the highest current values throughout the voltage range. This result shows that the doping concentration of 4% Mn provides an optimal doping concentration for charge transport and humidity sensing applications. At this concentration the balance between oxygen vacancy formation, carrier concentration and lattice stability seems to be the most favorable. The highest sensitivity and shortest response and recovery times observed for the 4% sample are consistent with the increased conductivity observed.

The higher current in the 4% Mn-doped sample can also be attributed to increased proton conduction under humid conditions. The adsorbed water molecules dissociate to form hydronium ions, which are involved in charge transport via the Grotthuss proton hopping mechanism [17]. This process is favoured by the higher availability of active adsorption sites in the optimally doped sample which results in improved electrical response [5].

When the concentration of Mn was increased beyond 4%, a decrease in current was observed. This reduction may be associated with the excessive defect formation, defect clustering and possible structural distortion in the ZnO lattice. Too many defects can act as traps for carriers. This reduces the mobility of charges and prevents efficient charge transport. Moreover, high concentrations of Mn may reduce the effective surface area for water adsorption and thus the proton conduction.

Optical absorption study

Optical properties of prepared Mn-doped ZnO thin films were studied by UV-Visible absorption spectroscopy. The UV-Visible absorption spectrum of the 4% Mn-doped ZnO thin film is shown in figure 4.

The absorption spectrum exhibits a strong absorption in the ultraviolet region and a relatively low absorption in the visible region, which is the characteristic feature of ZnO semiconductors. This behavior is mainly due to the wide band gap nature of ZnO. The high absorption in the ultraviolet region is due to the transitions of electrons from the valence band to the conduction band. As the energy of the photon approaches the energy of the band gap, a sharp rise in absorption is generated, which gives rise to the absorption edge in the spectrum.

An absorption edge was observed at about 385 nm. The optical band gap energy was estimated from the absorption edge wavelength using the relation:

$$E = \frac{hc}{\lambda}$$

where E is the band gap energy, h is Planck's constant, c is the speed of light and λ is the absorption edge wavelength [5,6].

The optical band gap energy of the 4% Mn-doped ZnO thin film was calculated to be about 3.22 eV using the observed value of the absorption edge. This value is slightly lower than the usual band gap of pure ZnO, which is usually reported to be around 3.30 eV. The observed decrease in band gap energy indicates modification of electronic structure of ZnO by incorporation of Mn.

This decrease in band gap energy may be attributed to the contribution of impurity levels and localized defect states in the forbidden energy gap. The incorporation of Mn ions into the lattice of ZnO may lead to the creation of extra electronic levels in the vicinity of the conduction or valence bands. These defect states lower the energy required for electronic excitation and thus lower the optical band gap. This decrease of the band gap is also associated with the formation of oxygen vacancies related to the incorporation of Mn [11].

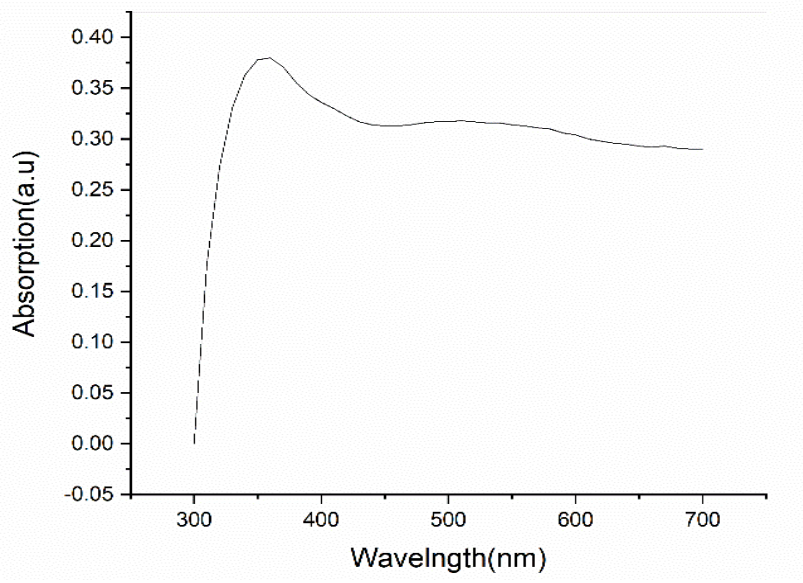


Figure 4: UV-Visible absorption spectrum of 4 % Mn-doped ZnO thin film

FTIR Spectroscopic Studies

Fourier Transform Infrared (FTIR) spectroscopy was used to study the chemical bonding, functional groups and molecular interactions in the fabricated Mn-doped ZnO thin films. Figure 5 shows the FTIR spectrum of 4% Mn-doped ZnO thin film.

Several distinctive absorption bands that corresponded to various vibrational modes were visible in the FTIR spectra of the 4% Mn-doped ZnO thin film. The broad absorption band observed around 3200-3600 cm^{-1} is attributed to O-H stretching vibrations. The broad peak indicates the presence of the hydroxyl groups and physically adsorbed water molecules on the surface of the thin film. The hydroxyl groups play a very important role in humidity sensing applications as they provide active sites for the adsorption of water molecules. The presence of these hydroxyl-rich surfaces enhances the proton conduction by the adsorption of water molecules and contributes greatly to the sensing mechanism [3, 18].

Another absorption peak which appears near 1600 cm^{-1} can be assigned to the bending vibration of H-O-H molecules. This peak further confirms the presence of adsorbed moisture on the ZnO thin film surface. Adsorbed water molecules are beneficial for humidity sensing as they can facilitate charge transport through proton hopping mechanisms. The O-H stretching and H-O-H bending vibrations indicate that the surface of the film has a high affinity for water adsorption, which is important for high humidity sensitivity [3].

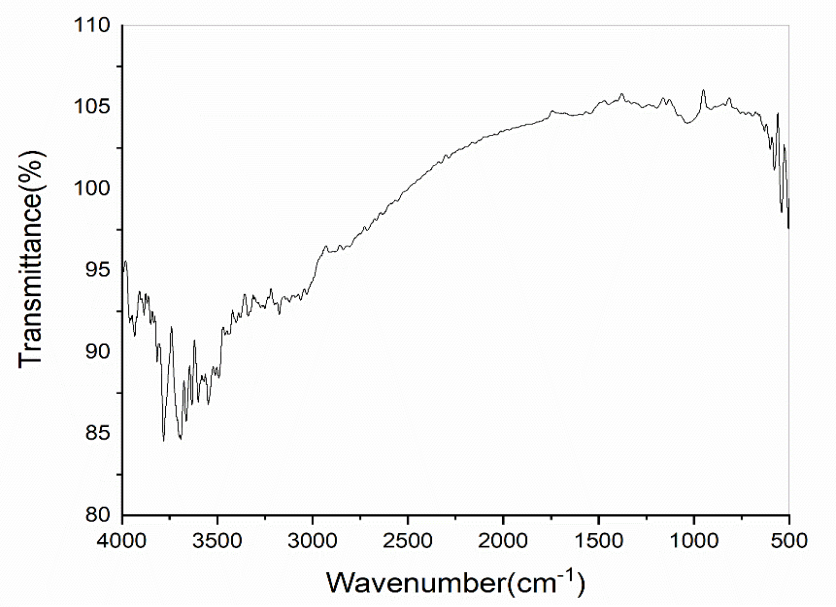


Figure 5: FTIR spectrum of 4% Mn-doped ZnO thin film

The absorption band in the low wavenumber region (ca. 500-600 cm^{-1}) was assigned to the Zn-O stretching vibrations. One of the important features of FTIR spectra is the presence of this peak which confirms the successful formation of ZnO in the fabricated thin films. The desired ZnO crystal structure has been successfully formed through the spin coating and annealing process as evidenced by the presence of the characteristic Zn-O absorption band [5].

The observed FTIR peaks suggest that the Mn-doped ZnO thin films fabricated contain structural Zn-O bonds and surface hydroxyl groups. Both these properties are directly related to the humidity sensing performance. The Zn-O network provides the semiconducting framework for

charge transport and the hydroxyl groups assist in the adsorption of water molecules and contribute to the electrical conductivity changes during sensing.

Conclusion

Mn doped ZnO thin films were fabricated on FTO glass substrates using sol-gel spin coating technique and humidity sensors were evaluated. All the films showed a decrease in electrical resistance with increasing relative humidity due to adsorption of water molecules. The 4% Mn-doped ZnO thin film showed the highest sensitivity, fastest response time and fastest recovery time compared to other investigated samples (0%, 2%, 4%, 6% and 8%). The current–voltage (I–V) characteristics showed ohmic behavior and highest current response was observed for 4% Mn-doped sample. Optical characterization shows a band gap of 3.22 eV which is less than the normal value of 3.3 eV for ZnO due to the presence of Mn. FTIR analysis confirmed the Zn-O bonding and presence of hydroxyl groups required for humidity sensing. The performance degraded with increasing Mn contents (6 and 8%) due to defect clustering and lattice distortion. Therefore, the spin coated 4% Mn-doped ZnO thin films are promising candidates for low-cost and high-performance humidity sensors for practical monitoring applications in agriculture, healthcare, food storage, and industrial process control.

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