

A review of Zinc Oxide-Tin Oxide (ZnO-SnO₂) Nanocomposite for Humidity Sensors

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ABSTRACT

This paper reviews the fabrication of zinc oxide-tin oxide (ZnO-SnO₂) nanocomposite in humidity sensors. ZnO and SnO₂ each had a wide energy band gap, making them suitable for producing high-quality humidity sensors. Also, ZnO and SnO₂ were the ideal heterojunctions with high sensitivity and thermal stability. In combination, the ZnO-SnO₂ nanocomposite was an n-type semiconductor with high versatility in many applications, such as gas sensors, lithium-ion batteries, and photocatalytic degradation. Besides, the nanostructure film of ZnO-SnO₂ was relatively easy to prepare and characterise while manipulating ZnO and SnO₂ could enhance device performances. Thus, the nanostructure of ZnO-SnO₂ would likely measure the humidity sensing performance.

Keywords: humidity mechanism, humidity sensor, nanocomposite, SnO₂, ZnO

1. INTRODUCTION

Humidity sensors play an important role in many industries and applications, such as pharmaceutical processing, medical health, meteorological monitoring [1], and food safety [2]. The photocatalytic property, gas sensing [3 - 4], and humidity sensing properties [5] of metal oxide have now generated considerable interest among scientists.

One of the ideal candidates of semiconductor metal oxides is zinc oxide (ZnO). Thus, studying the characteristics, structures, advantages, and methods of ZnO fabrication would help understand the suitability of ZnO at different conditions, such as at extreme environments, low-level humidity detection, and high humidity level. Besides, ZnO could be used for humidity sensors due to its wide specific surface area, high thermal stability, high electron mobility, and high oxidation. Also, it is economical [6 - 8].

Besides ZnO, tin oxide (SnO_2) is a good insulator with few carriers but is non-stoichiometric. It is an n-type semiconductor with a bandgap of 3.6eV, transparent, and conductive [9] because it has many charge carriers. Thus, SnO_2 is suitable for many applications, such as solid-state gas sensors, sensing, and measurement advanced sensors for power generation, optical-electronic devices, rechargeable Li batteries, solar cells, optical devices, and low emission glass due to its good optical, chemical, and electrical properties [10 - 12].

Titanium dioxide (TiO_2) is also semiconducting material with a bandgap ranging from 2.85 to 3.15 eV. Various applications that been used due to its high chemical stability, non-toxicity nature and wide bandgap. However, the sensing performances of TiO_2 generally suffer from insufficient long-time stability, high resistance, cross-selectivity and limited application [13]. The researcher investigated on ZnO/ TiO_2 composite by using sol-gel process. The comparison of pristine TiO_2 films, ZnO nanorods and ZTNA was considerably enhanced through coating of nanorod template with an anatase TiO_2 shell on humidity sensing performances. The response and recovery behavior of the substrate was not affected by the composition formation [13].

ZnO and SnO₂ are the best materials and commonly used in solar cells, gas sensors, and humidity sensors [14 - 15]. The manipulations of ZnO and SnO₂ can improve the performance of these sensors such as humidity sensor. Many researchers investigated the composite ZnO-SnO₂ using various methods, such as electrospinning, hydrothermal, and spin-coating. These studies indicated that fabricating the composition ZnO-SnO₂ on the ZnO layer to create double-layer films could improve the sensor's performance. Besides, the deposition of ZnO-SnO₂ showed good potential because of its wide bandgap. These films stabilise the humidity sensor substantially [16 - 19].

Meanwhile, there are many humidity sensors, such as humidity capacitors, thermal, and humidity-sensitive resistors. In general, a good humidity sensor possesses several important characteristics, i.e., low hysteresis, high sensitivity, fast recovery, and rapid responses. Other good characteristics of a humidity sensor include high thermal stability and long lifetime. Overall, a humidity sensor measures the quantity of water vapour present in the air. It calculates the atmospheric water vapour content as relative humidity and absolute humidity.

This paper reviews the ZnO-SnO₂ nanocomposites of the humidity sensor. These nanocomposites were fabricated into the humidity sensor using various methods, such as sol-gel, spin-coating, and electrospinning. The structural, optical, electrical, and humidity sensing performances of the nanocomposite films were discussed.

2. MECHANISMS OF HUMIDITY

Humidity is the quantity of water vapour present in a gas or a mixture of gases [20]. For example, nitrogen is a pure gas, but the air is a mixture of various gases. Humidity is commonly measured in units, such as relative humidity (rh), dew/frost point (D/FPT), and parts per million (PPM). rh is a ratio of the atmospheric moisture content to the maximum (saturation) vapour pressure of the gas at a given temperature [20]. In general, rh can be classified into semiconductor,

ceramic, and polymer. To better understand performance of a humidity sensor and the temperature effect, the relative sensing signal (S), response, and recovery durations of times were evaluated. Specifically, the relative sensing signal S of the sensor is given in Equation 1 below [20].

$$S = \left(\frac{R_a - R_{rh}}{R_a} \right) \times 100 \quad (1)$$

Where R_a is the resistance at 15% Rh and R_{rh} is the total resistance measured for the sensor. This describes the response time of adsorption or the recovery time of desorption for a sensor to reach a 90% change in the total resistance.

The sensitivity of the films to humidity (S_1) could be determined by Equation 2 below [21].

$$S = \frac{I_{90\% rh}}{I_{40\% rh}} \quad (2)$$

Where, $I_{40rh\%}$ is the sensor current at initial humidity level (40% rh) and $I_{90rh\%}$ is the sensor current at 90% rh. The response/recovery times are refer to the time taken for the film to reach 90% of current changes during adsorption/desorption processes [21].

Specifically, surface metal cations with high charge-carrier density will absorb the hydroxyl group of each water molecule. The electrostatic force will be strong enough to break one of the O-H bonds of the H_2O molecules, building a strong chemical bond between the metal and hydroxyl ions (M^+ and OH^-) [22].

At low humidity levels, the physisorbed layer is absent and only a chemisorbed layer is present. The chemisorbed is formed on the first contact with water vapour but is unaffected by changes in humidity. However, once the temperature increases, this layer will disappear due to the conduction of proton hopping between the hydroxyl groups. The primary source of charge carriers is derived from the proton released during the hydration of H_3O^+ . At high humidity levels, the protons between neighbouring water molecules hop more easily, and the

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transportation of charge carriers follows the Grotthuss chain reaction. The sensitivity of the sensor increases significantly along with the relative humidity. The proton conduction reactions for low (LH) and high humidity (HH) levels are given in Equations 3 and 4 [22], while Figure 1 shows the adsorption of water molecules on the nanocomposite surface of ZnO-SnO₂.

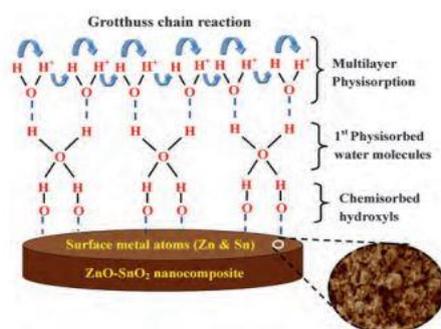
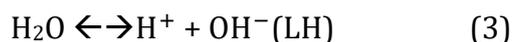


Figure 1 - The adsorption of water molecules on the surface of ZnO-SnO₂ nanocomposite [22].

3. HUMIDITY MATERIALS

Humidity sensing and control are especially important for various industrial fields and human life. The dominant functions of humidity sensors have traditionally been used for humidity control in heating, food packing, the manufacture of electronic equipment, and meteorology stations [20, 22]. Several researchers had developed a sensing device formed on nanostructural semiconductors of metal oxides with excellent chemical reactive surfaces that have water-absorbing, mechanical durability, and thermal stability [14, 21].

In a humidity sensor, a large surface area leads to a high performance of the sensor. Changes in the electrical signal in humidity are attributable to the adsorption of water molecules from the atmosphere on the surface of the sensing materials. Thus, large surface area and electron

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concentrations are beneficial to sense the change of humidity sensing in the humidity sensor due to the exposure of more active sites to the adsorbed water molecules [23].

In a study that investigated the optimum performance of humidity sensing devices at different Sn concentrations [23]. TZO was deposited on a seed layer-coated glass substrate by sonicated sol-gel immersion method. The result indicated that increasing the concentration of Sn, decreased the size of crystallite, diameter, and thickness of the nanoparticle [23]. Meanwhile, the ZnO-SnO₂ nanoparticle films were characterised using the spin-coating and immersion method [24]; the ZnO-based humidity sensor showed a minimum varying current, indicating that the composite structure strongly improved the sensor's performances.

In the investigation of the SnO₂ nanoparticles for humidity sensor via the sol-gel route [25], it was reported that the nanostructure of SnO₂ based thin film with leaf structure enhances feasibility for detecting humidity sensing. The humidity ranged from 10 to 90% rh, and the leaf-shaped SnO₂ showed high sensitivity 1.8 nW/% at room temperature. Besides, the colloidal SnO₂ nanowires on the humidity sensor were studied by spin-coating, and the high surface activity of SnO₂ nanowires worked effectively, with high sensitivity and fast response [26].

Also, ZnO nanosheets were synthesised on the aluminium (Al) layer with different Al thicknesses for humidity sensors [27]. The results indicated that reducing the thickness of the Al layer changed the ZnO structure from nanosheet to nanorod [27]. Besides, the sensor performance of Au-ZnO was examined using different concentrations of Au nanoparticles as a modifier [28]. When water molecules were adsorbed on the surface of the Au-ZnO nanosheets, more electrons reacted with x, thus enhancing the sensor performance. Table 1 shows the performances of humidity materials that researchers had studied.

Table 1 – Humidity materials.

Material	Performances	Methodology	References
TZO nanoarod arrays	3.36 (R_a/R_{rh})	Sol-gel	[23]
ZnO-SnO ₂ nanoparticle	90.60 (R_a/R_{rh})	Spin-coating, immersion	[24]
SnO ₂ nanoparticle	0.43 to 1.80nW/%RH	Sol-gel	[25]
SnO ₂ nanowires	1993 Hz	Colloidal	[26]
ZnO nanosheets	43.40 to 2.96% (10 ppm)	Nanogenerators (NG)	[27]
Au-ZnO nanosheets	3.00%	Hydrothermal	[28]

4. DEVICE CONFIGURATION

Currently, nanotechnology is one of the important technologies in the industries such as electronics, medicine, and agriculture. In this respect, metal oxides of ZnO and SnO₂ are one of the most versatile semiconductors [31 - 34] because they co are essential constituents in various devices, such gas sensor, humidity sensor [29 - 30], and lithium-ion batteries. Although there are studies on the fabrication and characterisation of ZnO and SnO₂ composite nanostructure, a few of them used ZnO and SnO₂ as humidity materials [35 - 39].

Besides, few studies were conducted on the heterostructure metal oxide for humidity sensing. In humidity sensors, a single-layer thin film is often associated with several disadvantages such as poor free carriers and possesses high resistive film. Also, although the combination of ZnO and SnO₂ has been widely used in gas sensors and solar cells, it is not commonly used in humidity sensors [21, 29], especially not when combined in a double-layer structure. Given that the

conduction band of SnO₂ is lower than ZnO, i.e., electrons would pass from ZnO to SnO₂ in the double-layer thin film, the ZnO and SnO₂ should improve the sensor's sensitivity.

The humidity performance of the ZnO films was examined in the preparation of the ZnO nanorod array via Fe-doping at low temperature using the sol-gel and spin-coating methods [21]. X-ray diffraction (XRD) showed that compared to ZnO, the size of crystallite and lattice constant of Fe-doped ZnO were smaller. Besides, the Fe-doped ZnO showed a smaller diameter around 10 nm and 85 nm at tip and middle parts, respectively with a lower thickness approximately 1.44 μm compared to ZnO. ZnO having averages diameters of 105 nm and thickness approximately 1.51 μm, respectively. The Fe-doped ZnO showed good electrical property with quick response and fast recovery time, i.e., it had good potential in sensing.

Figure 2 shows the surface response of SnO₂-ZnO in the absence and presence of humidity. The characteristics of SnO₂-ZnO, such as structural, electrical, and humidity sensing performance at different times of SnO₂ deposition had been well studied by the methods spin-coating and immersion [24]. When ZnO was deposited with SnO₂, the surface area increased. However, the grain and crystallite decreased in size owing to the increment of the SnO₂ thickness. The fabrication of ZnO-SnO₂ on the ZnO layer created double-layer films to improve the sensor's performance [24].

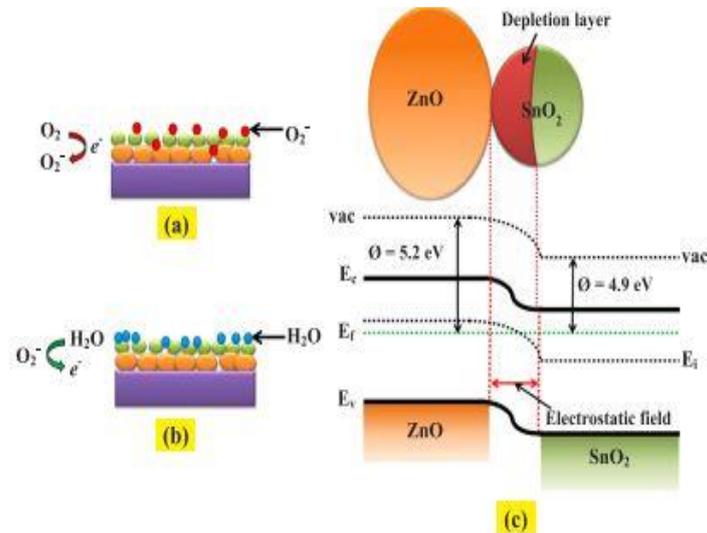


Figure 2 - The surface reaction of ZnO-SnO₂: (a) in the absence of humidity, (b) in the presence of humidity, and (c) the energy band of ZnO-SnO₂ [24].

In another study that investigated the application of humidity sensors on high sensitivity over varying humidity levels using the sol-gel method [29], the hierarchical Sn-doped ZnO nanorod was fabricated. XRD revealed that the Sn-doped ZnO showed slightly higher intensity than the undoped ZnO. Compared to the undoped ZnO, the Sn-doped ZnO had a smaller crystallite size, diameter, and thickness but with higher sensitivity. Figure 3 shows the water adsorption on the surface of the ZnO nanorod.

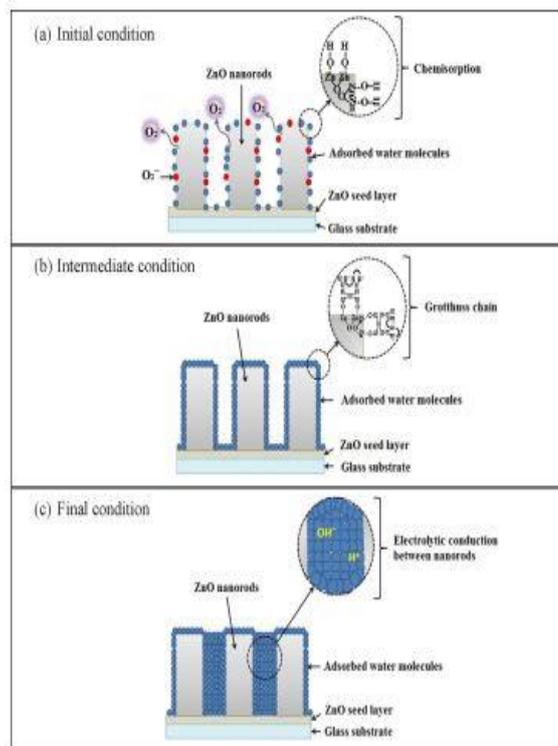


Figure 3 - Water adsorption on the surface of ZnO nanorod: (a) at 40% RH (initial stage), (b) at the average between 40to 90% RH, and (c) at 90% RH (the final level of humidity) [29].

5. CONCLUSION

This review discussed how the humidity sensor depended on the deposition of (ZnO)-SnO₂ nanocomposite. Besides, the mechanism of the humidity sensor on metal surfaces was examined.

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In this paper, the use of ZnO-SnO₂ as metal oxide humidity sensor is presented in detail. The deposition of ZnO-SnO₂ showed good potential as a humidity sensor. Furthermore, the properties that had been reviewed in this paper are structural, optical and electrical including sensitivity, reaction time and stability. In general, ZnO and SnO₂ were widely used in many industries or devices, such as rechargeable Li batteries, thermal, optoelectronic and solar cells. Thus, further studies on fabricating ZnO-SnO₂ nanocomposites onto humidity sensors are essential.

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