International Journal of Nanoelectronics and Materials
Volume 16 January 2023 [11-19]

A Review of Zinc Oxide-Tin Oxide (ZnO-SnO_2) Nanocomposite for Humidity Sensors

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Received 20 July 2021, Revised 27 April 2022, Accepted 24 June 2022

ABSTRACT

This paper reviews the fabrication of zinc oxide-tin oxide (ZnO-SnO_2) nanocomposite in humidity sensors. ZnO and SnO_2 each has a wide energy band gap, making them suitable for producing high-quality humidity sensors. Also, ZnO and SnO_2 are the ideal heterojunctions with high sensitivity and thermal stability. When combined, ZnO-SnO_2 nanocomposite is 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-SnO_2 is relatively easy to prepare and characterise while manipulating ZnO and SnO_2 could enhance device performances. Thus, the nanostructure of ZnO-SnO_2 would likely measure the humidity sensing performance easily.

Keywords: Humidity mechanism, humidity sensor, nanocomposite, SnO_2, 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 to 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, as well as economical [6 - 8].

Apart from 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

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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 have used it 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]. Previous researchers 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 behaviour of the substrate was not affected by the composition formation [13].

ZnO and SnO_2 are the best materials and commonly used in solar cells, gas sensors, and humidity sensors [14-15]. The manipulations of ZnO and SnO_2 can improves the performance of these sensors such as humidity sensor. Many researchers investigated the $ZnO\text{-}SnO_2$ composite using various methods, such as electrospinning, hydrothermal, and spin-coating. These studies indicated that fabricating the composition $ZnO\text{-}SnO_2$ on the ZnO layer to create double-layer films could improve the sensor's performance. Besides, the deposition of $ZnO\text{-}SnO_2$ 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 $ZnO\text{-}SnO_2$ 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 the 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 [20]:

$$S = \left(\frac{Ra - Rrh}{Ra} x100\right) \quad (1)$$

where Ra is the resistance at 15% Rh and Rrh 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) could be determined by Equation 2 [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 referring 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 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-SnO_2.

$$H_2O \leftarrow\rightarrow H^+ + OH^-(LH) \quad (3)$$

$$2H_2O \leftarrow\rightarrow H2O^+ + OH^-(HH) \quad (4)$$

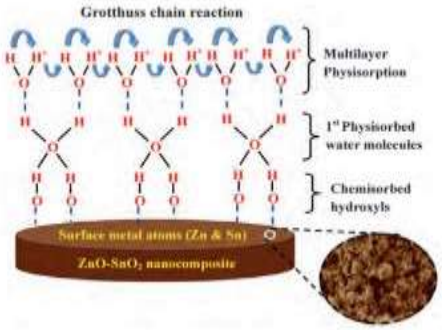

Figure 1. The adsorption of water molecules on the surface of ZnO-SnO_2 nanocomposite [22].

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 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, 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 will decreased the size of crystallite, diameter, and thickness of the nanoparticle [23]. Meanwhile, the ZnO-SnO_2 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 SnO_2 nanoparticles for humidity sensor via the sol-gel route [25], it was reported that the nanostructure of SnO_2 based thin film with leaf structure enhances feasibility for detecting humidity sensing. The humidity ranged from 10 to 90% rh, and the leaf-shaped SnO_2 showed high sensitivity 1.8 nW/% at room temperature. Besides, the colloidal SnO_2 nanowires on the humidity sensor were studied by spin-coating, and the high surface activity of SnO_2 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 (Ra/Rrh)	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 SnO_2 are one of the most versatile semiconductors [31-34] because they 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 SnO_2 composite nanostructure, a few of them used ZnO and SnO_2 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 SnO_2 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 SnO_2 is lower than ZnO, i.e., electrons would pass from ZnO to SnO2 in the double-layer thin film, the ZnO and SnO_2 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-dope ZnO showed good electrical property with quick response and fast recovery time, i.e., it had good potential in sensing.

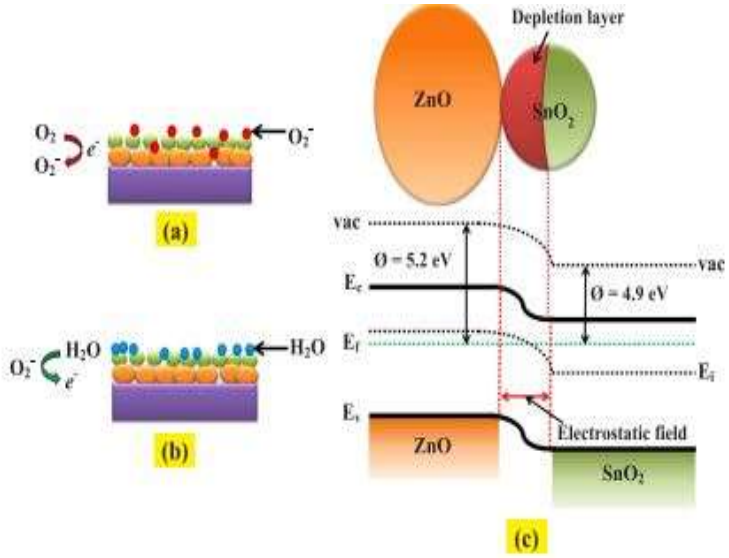

Figure 2. The surface reaction of ZnO-SnO_2: (a) in the absence of humidity, (b) in the presence of humidity, and (c) the energy band of ZnO-SnO_2 [24].

Figure 2 shows the surface response of SnO_2-ZnO in the absence and presence of humidity. The characteristics of SnO_2-ZnO, such as structural, electrical, and humidity sensing performance at different times of SnO_2 deposition had been well studied by the methods spin-coating and immersion [24]. When ZnO was deposited with SnO_2, the surface area increased. However, the grain and crystallite decreased in size owing to the increment of the SnO_2 thickness. The fabrication of ZnO-SnO2 on the ZnO layer created double-layer films to improve the sensor's performance [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.

5. CONCLUSION

This review discussed how the humidity sensor depends on the deposition of ZnO-SnO_2 anocomposite. Besides, the mechanism of the humidity sensor on metal surfaces was examined. In this paper, the use of ZnO-SnO_2 as metal oxide humidity sensor is presented in detail. The deposition of ZnO-SnO_2 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 SnO_2 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.

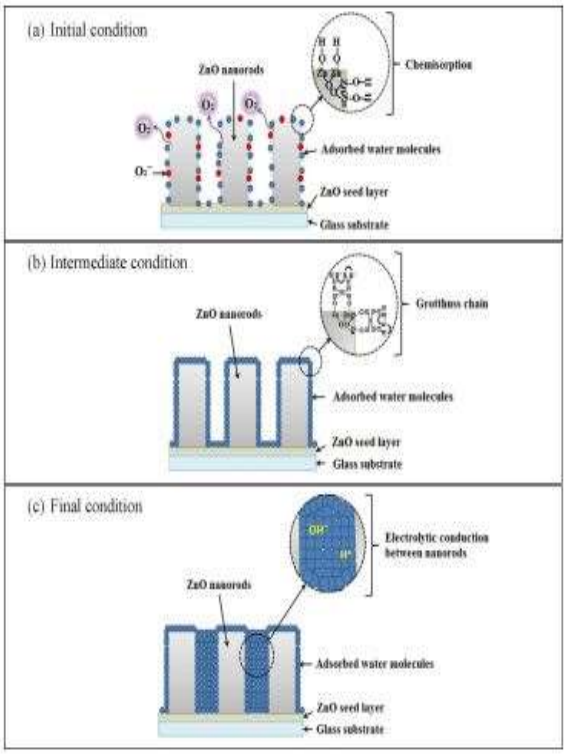

Figure 3. Water adsorption on the surface of ZnO nanorod: (a) at 40% RH (initial stage), (b) at the average between 40to 90% RH, and (c) at 90% RH (the final level of humidity) [29]

ACKNOWLEDGEMENTS

The author would like to the employees of NANO-ElecTronic Centre kindly helped in completing the experimental work. Thanks also to Research Management Centre (RMC), Universiti Teknologi MARA (UiTM) and Ministry of Higher Education (MOHE) for financial support (600-IRMI/FRGS RACER 5/3 (010/2019).

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