# CHAPTER 4

## ZnO Tetrapods Network Applied as Room Temperature Gas Sensor

Gas sensors had been attracted much attention due to their potential applications in environmental safety, industrial safety, and health monitoring [55, 56]. The metal oxide that was wide band gab semiconductor, gas sensor devices had been invented since 1960s, which via $SnO_2$ as gas sensing material. The $SnO_2$ sensor device was prepared by thick film technology for fabrication to use in gas leakage alarm application[42]. Even though, the $SnO_2$ gas sensors were extensively studied. Though, it had some limit to further improvement as few selectivity, sensibility in ppb level range, long recovery and response time, high working temperature, etc. [42, 56, 58-60]. As a result, ZnO was choice option for gas sensor device applications. ZnO had an appealing property within the scientific communal as a smart material and it still had more good attention potentials, and sensor devices [42, 56, 58-60].

Among semiconductor metal oxides, ZnO had been widely used in gas-sensing applications because of its good response to a diversity of oxidizing or reducing gases at high temperature, photo-activated gas sensing for room temperature, inexpensive and being friendly to the surroundings [42, 56, 58-60]. The main problem of gas sensors used in nowadays was that they work at high temperature. This causes high power consumption and limits their application such as detecting flammable gas. Therefore, many attempts had been made to discover gas sensors with low working temperature.

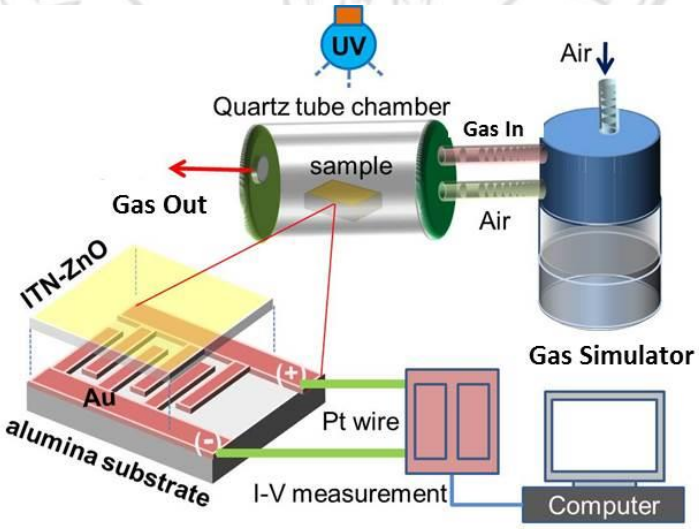
ZnO based gas sensors also had good response to ethanol and acetone than others gas [53, 92]. In addition, ZnO with had structures different such as nanofibers[93, 94], dumbbell-like[95, 96], nanorod[97], and tetrapod[98], that had been improved the sensitivity, stability and decrease the operating temperature to room temperate[99] that it application in smart phone and sensor miter because it saved energy and was not hazardous when near flammable gases. Tetrapod-shaped ZnO is an interesting structure

since it was found to display a fantastical optical property and it has improved gas-sensing properties at low temperature. The gas sensitivity was high, recovery time and response time was rapid because tetrapod-shaped ZnO had more porous structure. It has higher specific the surface area. When tetrapod network well response with Ultraviolet (UV)[70], tetrapod ZnO structure that was connected network structure seems to be increase effective response properties of gas sensors

In this work, ITN-ZnO has also exhibited unexpectedly properties of electrical and gas sensing properties compared to other morphologies of ZnO. Then, we have fabricated the ITN-ZnO sensors used as ethanol and acetone sensing devices at room temperature.

### 4.1 Fabrication of gas sensor

Fabrication of sensors ITN-ZnO, ZnO tetrapods (T-ZnO), and zinc oxide powder (P-ZnO); 99.9%, Sigma-Aldrich, less than 1 μm in particle size) were mixed in ethanol and screened on alumina substrates with gold interdigital electrodes as shown. Pt wires were then used to connect them with the Au electrodes, and the samples were put in the gas chamber under UV radiation measurement, as shown in **Fig. 4.1.**




**Figures 4.1** The schematic illustration of the sensor and the measurement system used for gas sensing. Pt wires were connected to electrodes and put in the quartz tube chamber with UV lamps. UV light source (λ = 365 nm; UVA) with intensity of

2.80 mW/cm$^2$ was used. I-V characteristics were measured with a dc voltage and current sources which were interfaced and controlled by a computer in air and nitrogen ambient with UV on/off illumination. To characterize the ethanol and acetone sensing properties, the ethanol vapor with concentration of 0-1000 ppm was operated to ITN-ZnO sensor at operating temperature from room temperature to 500$^o$C under UV illumination. Reprinted with permission from ref [70]. Copyright (2015) American Chemical Society.

## 4.2 Ethanol sensing properties of different ZnO morphologies

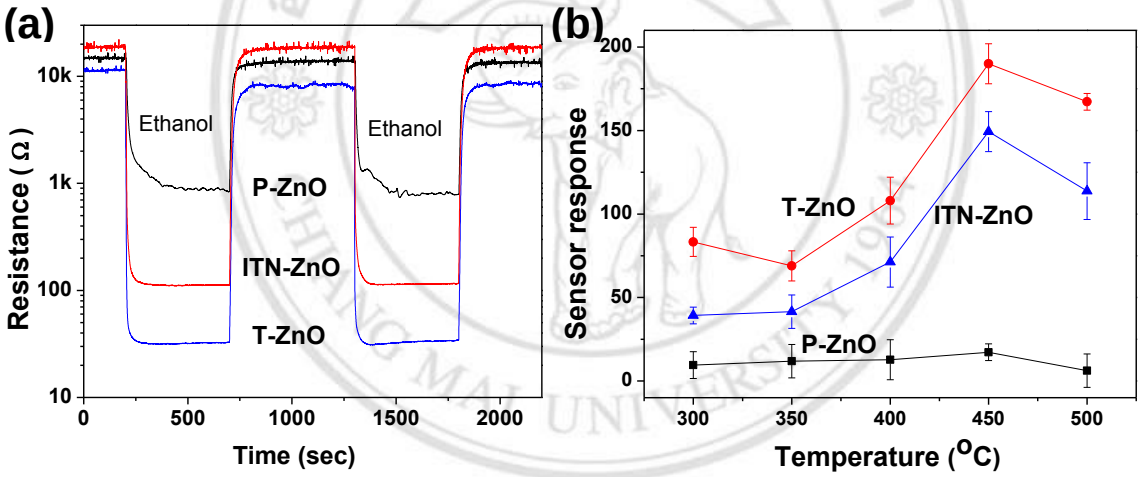



**Figure 4.2** (a) The plot of two cycles of resistance change under ethanol ambient that at ethanol concentration of 1000 ppm for gas sensor based on different ZnO morphologies at operating temperature of 450°C. (b) The plot of sensor response that ratio of resistance measured in air to in ethanol vapor concentration of 1000 ppm at various operating temperatures. Reprinted with permission from ref [70]. Copyright (2015) American Chemical Society.

The different ZnO morphologies that result of the ethanol sensing properties of devices are investigated. Two cycles in the **Fig. 4.2(**a) was shown of resistance change under ethanol ambient that at concentration of 1000 ppm for sensor based on different ZnO morphologies at operating temperature of 450°C. It can be seen that the sensor

resistance rapidly reductions when ethanol vapor was released into the chamber, and the resistance value returns back to the original resistance when ethanol vapor was removed from the chamber. These point toward that the nanostructured ZnO had the sensing properties and were applicable for ethanol sensor.

The sensor response that ratio of resistance measured in air to in the ethanol vapor at concentration of 1000 ppm was plotted in the **Fig. 4.2(b)** as a function of operating temperatures. The sensor response property depends on ZnO morphology, and the highest sensor response was observed in T-ZnO device sensor. This proposes that, at high operating temperature, the ITN-ZnO sensor exhibited different ethanol sensing properties to the other ZnO morphologies.

From the directly above discussion, in order to get further understandings into the electrical and gas sensing properties related to the morphology of ZnO nanostructured, the combined effect of UV light and ethanol vapor on the device characteristics had been investigated. Therefore, ethanol sensing properties under UV illumination are investigated at room temperature and at different operating temperatures. It was value noting that thermal energy was not required ever since UV radiation was used as an alternative for conduction band electron excitation. The ITN-ZnO sensor resistance under UV illumination in air and in ethanol vapor at room temperature was plotted as a function of time as presented in the **Fig. 4.3(a).** The resistance (conductance) of ITN-ZnO sensor device fast decreases (increase) because of the increase of photoelectrons by the photon absorption and an electron excitation from the valence band to the conduction band.

After the Ultraviolet a (UVA) irradiation was intercept down, the sensor resistance returns back to the original value resistance. Though, when the ethanol vapor was released in the chamber, the ITN-ZnO sensor resistance amazingly increases which was reverse to the sensor case at high operating temperature. For typically, the resistance increase under ethanol vapor directs p-type behavior of ZnO semiconductor. Moreover, the result from experiment the increase in resistance and sensor response depends on the ethanol concentration was shown in the **Fig. 4.3(b)** from 10-1000 ppm. This proposes the possibility for innovative application as gas sensor operating at room temperature.

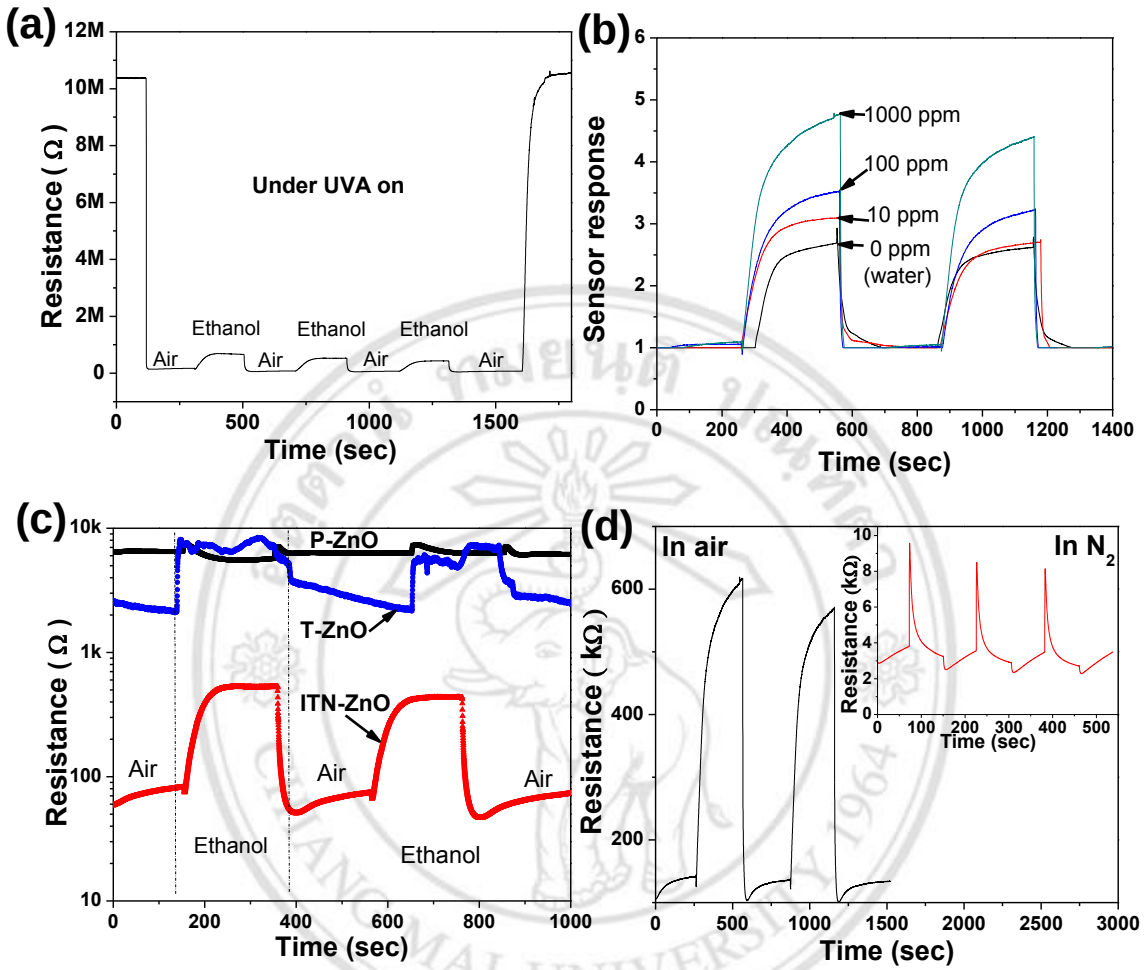



**Figure 4.3** (a) The resistance change of ITN-ZnO sensor tested under UV light illumination in air and in ethanol ambient that concentration of 1000 ppm as a function of time at room temperature (RT). (b) At RT, sensor response properties and ethanol concentration of 10-1000 ppm. (c) ITN-ZnO sensor resistance change in comparison with T-ZnO and P-ZnO ones tested under UV light at RT and ethanol concentration of 1000 ppm. (d) ITN-ZnO sensor resistance change under UV light at RT and ethanol concentration of 1000 ppm experienced in air along with an inset presentation the resistance tested in nitrogen ambient. Reprinted with permission from ref [70]. Copyright (2015) American Chemical Society.

Comparison the sensors constructed from P-ZnO, T-ZnO and the ITN-ZnO sensor shown superior ethanol sensing properties under UV light at room temperature than

those of twain T-ZnO and P-ZnO sensors as seen in the **Fig. 4.3(c).** To know the effects of oxygen molecules in the air and on the ethanol gas sensing characteristics, the ITN-ZnO device sensor resistance monitored in the air was compared with that measured in nitrogen ambient as shown in the **Fig. 4.3(d).** It could be seen that the improved resistance in nitrogen was much lesser than that of in the air. This proposes that oxygen molecules play a significant role to the ethanol vapor sensing mechanisms at room temperature.

### 4.3 Acetone sensing properties of different ZnO morphologies

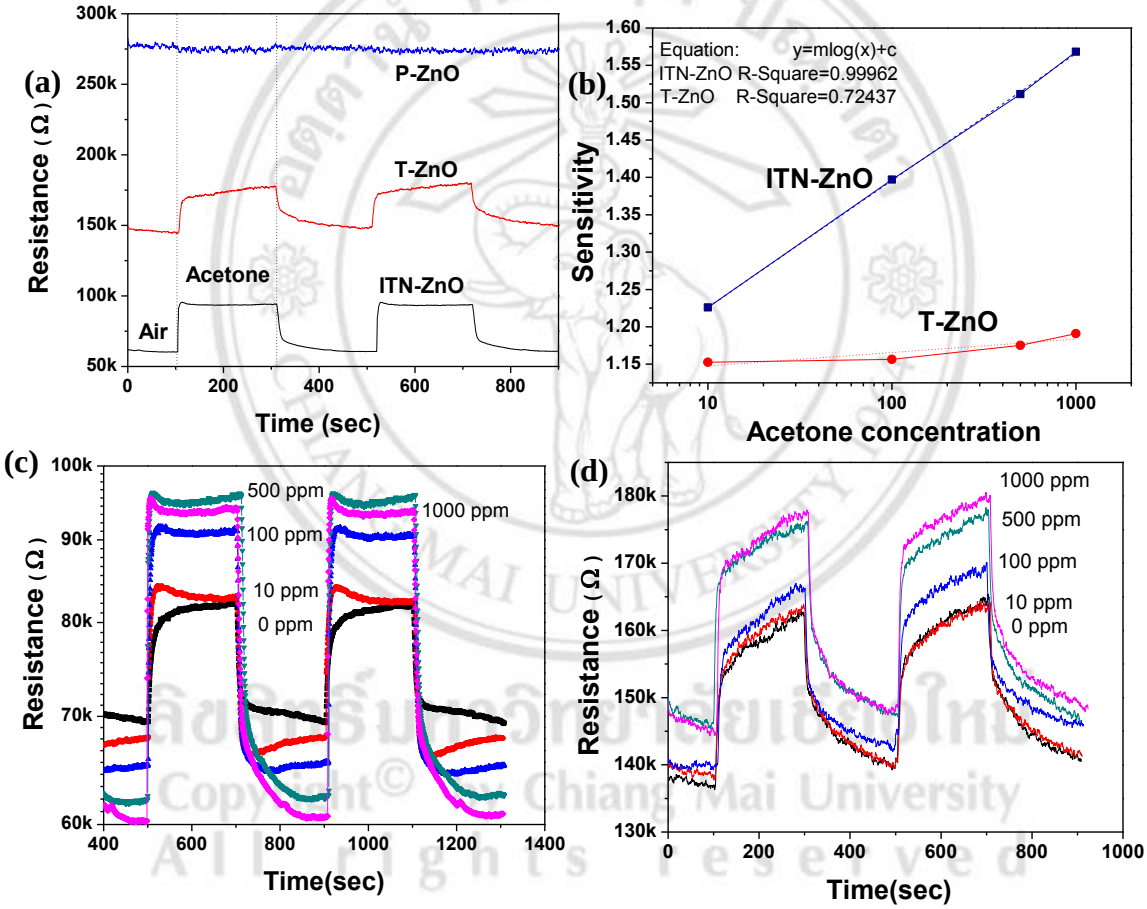



**Figure 4.4** (a) Gas sensing responses of the ITN-ZnO to 1000 ppm of acetone under UV radiation at room temperature compared with that of T-ZnO and P-ZnO. The typical responses were shown for (c) ITN-ZnO and (d) T-ZnO sensor under various concentrations. (b) The corresponding sensitivity of the sensors response in (c) and (d) against acetone concentration.

Under UV radiation, the resistances of all samples were decreased and significantly different in each sample. ITN-ZnO had less resistance than others. The resistance of ITN-ZnO and T-ZnO sensor increased after exploding acetone gas and recovered to former value (baseline) when turned acetone gas off whereas P-ZnO did not response to acetone gas, as seen **Fig. 4.4(a).** Typical responses of ITN-ZnO and T-ZnO sensor for various concentrations are shown in **Fig. 4.4(c) and (d)**, respectively. The higher concentration resulted in the more response. Both sensors have different characteristic response. The resistance of T-ZnO sensor rapidly increased in the first few second and then gradually increased as time evolution but that of ITN-ZnO sensor rapidly increased at first and then saturated. Similar characteristic occurred in the repetition. The sensitivity, ratio of resistance in gas ($R_g$) to resistance in air ($R_a$), of both samples increased as a function of acetone concentration, as seen in **Fig. 4.4(b)**, but that of ITN-ZnO was higher than T-ZnO significantly.

### 4.4. Gas sensing mechanisms

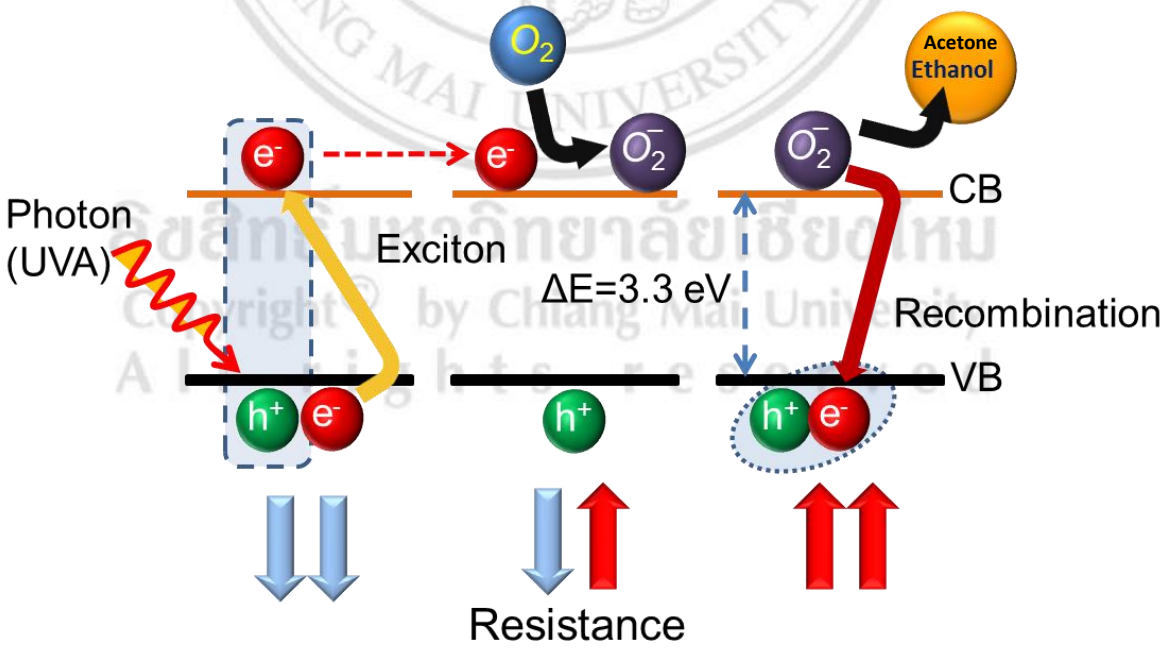



**Figure 4.5** Schematic illustrations for ethanol/acetone sensing mechanisms that can be used to illustrate the resistance increase under ethanol/acetone vapor at room

temperature. There are four stages for sensing mechanism such as oxygen adsorption, photoelectron generation, oxygen-ethanol/acetone reaction, and free electrons release back to valence band. Reprinted with permission from ref [70]. Copyright (2015) American Chemical Society.

As a result, the sensor resistance increase can be explained the detail by using the ethanol/acetone vapor sensing mechanism process at room temperature as sketched in the **Fig. 4.5.** The proposed sensing mechanism process was composed of four phases. Firstly, under UV light, photoelectrons were generated from the photo-excited electrons in the valence band (VB) to the conduction band (CB) of semiconductor using UV absorption, resulting to the decrease in sensor resistance in UV light. Secondly, oxygen molecules in the air trap the electrons on the surface, and then forming superoxide radicals ($O_2^-$). At this phase, the sensor resistance of the ZnO sample increases because of loss of photoelectrons in the conduction band (CB) and results to medium resistance compared with the first phase. This medium resistance could be confirmed by the sensor lower resistance measured in the air (130 kΩ) in comparison with that sensor resistance in nitrogen atmosphere (2.8 kΩ). The third process was related to the ethanol/acetone vapor oxidation by superoxide extremists, and then producing for free electrons. Typically, at high temperature, the free electrons release return back to the conduction band (CB) due to there were still many the available the conduction band states, resulting to the sensor resistance decrease as seen in the **Fig. 4.2(a).** However, there were much a lesser amount of available conduction band (CB) states compared with ones at high temperature (low probability according to a simple Boltzmann distribution) at room temperature. Thus, we suggested the fourth phase that the free electrons inject return back to the valence band with high probability by recombining with holes again in valence band and causing to the increase in sensor resistance. So, the sensor resistance increase could be primarily explained by the lack of photoelectrons or electron that returns back to the conduction band.

It was worth noting that sensor work at high operating temperature the ethanol/acetone sensor response was lower for the case of with and without UV light due to the thermal-excited electrons of sensor dominate in this case. Then, the ITN-ZnO that fabricated to be sensor was one of an exciting morphology of ZnO that could lead

to a lot of new applications because of its novel properties. Since the ITN-ZnO could be got by the simple and rapid synthetic process by microwave-assisted thermal oxidation, up-scale mass production processes of this ITN-ZnO nanostructure would be easily performed and as well increase feasibility for the device fabrication at low cost.

### 4.5. Chapter Summary

The ITN-ZnO also all at once exhibits superior electrical properties and gas sensing properties when compared with P-ZnO and T-ZnO. With the advantage of its improved transport partway for an electron transport to the electrode, room temperature gas sensor with improved performance was obtained. Therefore, the ITN-ZnO was one of an attractive morphology of ZnO structure that can lead to a lot of new applications because of its novel properties.