



Enhancement of sensor response by TiO₂ mixing and Au coating on ZnO tetrapod sensor

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ABSTRACT

The sensors based on ZnO tetrapods (T-ZnO) and ZnO tetrapods with TiO₂ mixing (T-TiZnO) and Au coating (Au/T-TiZnO) were investigated. The T-ZnO and T-TiZnO were synthesized by a simple thermal oxidation technique. The leg of the tetrapod is about 1–10 μm in length and 160–500 nm in diameter. Au coating was performed by sputtering technique and annealed at 550 °C for 6 h under normal atmosphere. The ethanol sensor response of the T-ZnO, T-TiZnO and Au/T-TiZnO sensors was tested at the operating temperature of 260–360 °C with the ethanol concentration of 50, 100, 200, 500, and 1000 ppm. It was found that at the optimum temperature the Au/T-TiZnO sensor exhibited the highest sensor response and the T-TiZnO sensor exhibited higher sensor response than that of the T-ZnO sensor. The Au/T-TiZnO sensor exhibited the highest sensor response up to 240 at 340 °C under the ethanol concentration of 1000 ppm. The enhancement of the sensor response based on the T-ZnO by TiO₂ mixing and Au coating can be explained by alloying effect and metal catalytic effect, respectively. The response enhancement can be explained in terms of electron concentration, n_0 in air and reaction rate constant, k_{Eth} . The evidence for both effects can be found in higher sensor resistance in air and lower sensor resistance in the ethanol ambient.

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1. Introduction

Gas sensors have been considered as a potential device for detecting flammable and toxic gases. They play an important role in medical diagnosis, environment safety, human traffic safety, and quality control in food, agriculture, and automotive industries [1–11]. Up to now, quasi one-dimension nanostructures (1D) including nanotubes [9,10], nanobelts [5], nanowires [4,8,12], and nanorods [7,13] with high surface-to-volume ratio have gained much interest as gas sensor materials. Several works have been reported on gas sensing properties of 1D metal-oxide semiconductor nanostructures such as SnO₂ [3–5,8], WO₃ [14], TiO₂ [15,16], In₂O₃ [12]. ZnO has also been studied because it is chemically and thermally stable [2,6,17]. Generally, the requirements of gas sensors are fast response, short recovery time, long-term stability, inexpensive, good selectivity, and high sensor response. It is well-known that the sensor response is affected by many factors such as operating temperature, concentration of test gas, surface adsorbed

oxygen species, sensor material size, material morphology, and so on [7,11,13,18].

In order to improve the sensor response, many techniques have been introduced. Sensor materials with nanostructures providing the large reactive surface have been widely studied and found to exhibit high sensor response. However, it is difficult to control the growth of nanomaterials with a desired size and a uniform shape. In addition, several studies were focused on metal catalytic effect of noble metals such as Ag [19], Au [5–7,18], Pt [14], and Pd [20,21]. Adding these metal catalysts as coatings on the sensor surface or by mixing with raw materials, the sensor response has been reportedly improved. Very recently, we have studied the enhancement of ethanol sensor response of Au-doped ZnO nanowires/belts by mixing Au with a raw material [18]. In a similar case, Li et al. reported an ultrahigh ethanol sensor response based on ZnO nanorod sensor modified by Au coating technique, and the reduction of response and recovery time were also observed [7]. Similarly, SnO₂ nanowires and nanobelts studied by Kolmakov et al. also showed the effect of Pd catalyst for the enhancement of the sensor response [21].

It has been reported that introducing some metal elements such as Ti, Ru, and Al together with host nanomaterials can improve and adjust the sensor response [2,11,22,23]. Previously, we have reported the ethanol sensing properties of the ZnO tetrapods (T-

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ZnO) alloying with TiO₂ prepared by a simple thermal oxidation technique. The sensor response improved with the addition of Ti into ZnO lattice which gave higher response than that of the undoped sample [11].

In this paper, we report the enhancement of the ethanol sensor response by TiO₂ mixing and Au coating on ZnO tetrapod sensors. These two simple techniques can significantly improve the sensor response of the ZnO tetrapod sensor. The enhancement of the sensor response can be empirically explained by using sensor response formula for the ZnO sensor in terms of electron concentration n_0 in air, due to alloying effect, and reaction rate constant k_{Eth} , due to catalytic effect, respectively.

2. Experimental

ZnO tetrapods mixing with TiO₂ (T-TiZnO) were synthesized by the simple thermal oxidation method [11]. Zn with 30 mol% of TiO₂ powder was mixed, and ground in agate mortar for 2 h. Then, the mixed powder in the amount of 2 g was loaded into an alumina crucible and put in the center of a furnace at a temperature of 1000 °C under normal atmosphere. After a few minutes of reaction, the alumina crucible was taken out from the furnace, and the white wool products were observed. The synthesized products were characterized by a field emission scanning electron microscope (FE-SEM), energy dispersive X-ray spectrometry (EDS), transmission electron microscope (TEM), and X-ray diffractometer (XRD) for morphology, chemical composition, phase formation, and crystal structure.

T-TiZnO was fabricated as an ethanol sensor (called T-TiZnO sensor) for alcohol breath analyzer by mixing with polyvinyl alcohol, and then pasted onto the alumina substrate (15.4 mm × 7.0 mm) with Au inter-digital electrodes. The sensing area was about 8.0 mm × 7.0 mm. The T-TiZnO sensor was dried in air for 1 day, annealed at 550 °C under normal atmosphere for 12 h, and then cooled down naturally to room temperature. After that, Au was coated onto the sensor surface for 3 s by sputtering technique. The Au-coated sensor (called Au/T-TiZnO sensor) was taken out from the sputtering chamber, and then subsequently annealed at 550 °C for 6 h under normal atmosphere. For Au/T-ZnO sensor, the coating amount of Au on the sensor material is clarified as the film thickness. We have measured the Au thickness coating on glass substrate using Rutherford Backscattering Spectrometry (RBS). The RBS spectrum of 3 s coating time (not shown here) was fitted using simulation program (SIMNRA), and it was found that the Au thickness is about 1.4 nm or about 8.5×10^{15} atoms/cm².

The ethanol sensor response of the T-ZnO, T-TiZnO and Au/T-TiZnO sensors was measured using a volt-amperometric technique, with an applied voltage of 5 V. The sensors were tested at the operating temperature of 260–360 °C with the ethanol concentration of 50, 100, 200, 500, and 1000 ppm. Since application as an alcohol breath analyzer is our goal, the ethanol vapor with different concentrations was generated from ethanol solutions using alcohol simulator (GUTH laboratory Inc., Harrisburg USA) at 34 °C. The alcohol simulator functioned to simulate alcohol concentration at conditions similar to an exhaled human breath. In general, the ethanol sensor response of sensor was determined from the change of sensor resistance. The ethanol sensor response is defined as $S = R_{air}/R_{gas}$ [11,17], where R_{air} is the electrical resistance of the sensor in air, and R_{gas} is its resistance in ethanol–air mixed gas.

3. Results and discussion

3.1. Sensor material characterization

After cooling down naturally in air for a few hours, the T-TiZnO was analyzed using XRD, and the typical XRD pattern was observed,

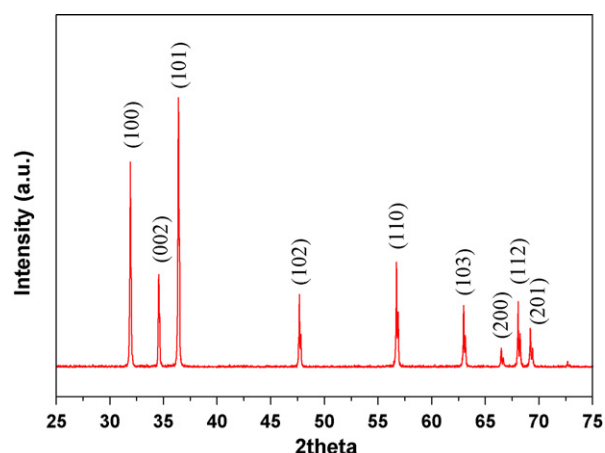


Fig. 1. Typical XRD pattern of the T-TiZnO synthesized at 1000 °C under normal atmosphere.

as shown in Fig. 1. All peaks on the pattern showed sharp peaks and can be indexed to a hexagonal wurtzite ZnO structure [11]. No other impurity peak was observed in the pattern. This pattern is similar to ZnO powder (not shown here). The lattice parameter a and c of the observed tetrapods are about 3.243 and 5.180 Å, respectively. The lattice parameters of the tetrapods are slightly smaller than that data in the standard file (JCPDS no. 36-1451, $a = 3.249$ Å and $c = 5.206$ Å). The contraction of lattice parameters by alloying with TiO₂ and MgO in Ti_xZn_{1-x}O [24] and Mg_xZn_{1-x}O [25,26] were also observed. This may suggest that mixing TiO₂ with Zn resulted in alloying effect.

Fig. 2 shows the FE-SEM micrographs of the T-TiZnO. As indicated in Fig. 2(a), the synthesized product consists of large amount of small size tetrapods with four symmetric legs. The leg of the tetrapod is about 1–10 μm in length and 160–500 nm in diameter. The high magnified FE-SEM image as shown in an inset of Fig. 2(a) showed that the tetrapod exhibits a needle-like structure with a hexagonal tip.

The chemical composition of the T-TiZnO was investigated using the EDS with the spot size in an order of micrometer. The EDS spectrum composed of Zn, Ti, and O elements as displayed in Fig. 2(b). The average atomic percent of Ti is less than 1% while that of Zn and O are about 48% and 51%, respectively. The atomic percent of chemical compositions of the tetrapod was identified from computer software using INCA suited v.4.06, Oxford instrument. The EDS analysis is only qualitative analysis with less accuracy compared to other method. However, this result implied that Ti was incorporated with ZnO in the tetrapod. For quantitative analysis, another technique will be needed such as inductive coupled plasma mass spectroscopy (ICP-MS).

Selected area electron diffraction (SAED) performed on a selected leg of the tetrapod was shown in Fig. 2(c). It is clearly seen that the SAED displayed a spot pattern indicating that the tetrapod exhibits single crystal property corresponding to the wurtzite ZnO structure. Moreover, only the spot pattern corresponding to the wurtzite hexagonal structure was observed indicating that there was no structural change due to mixing ZnO with TiO₂. This suggests the TiO₂ alloyed with ZnO, which is also consistent with the XRD result. Since Ti⁴⁺ has ionic radius of 0.068 nm which smaller than that 0.074 nm of Zn²⁺, Ti⁴⁺ trends to substitute into Zn²⁺ sites forming Ti_xZn_{1-x}O alloy [24]. From trace analysis, the T-TiZnO exhibits a growth direction along [0002] which is a typical growth direction for the ZnO tetrapods [11,27]. The effect of TiO₂ alloying with ZnO tetrapod structure was also observed in the Raman spectrum as discussed in our previous work [11]. The alloying effect is

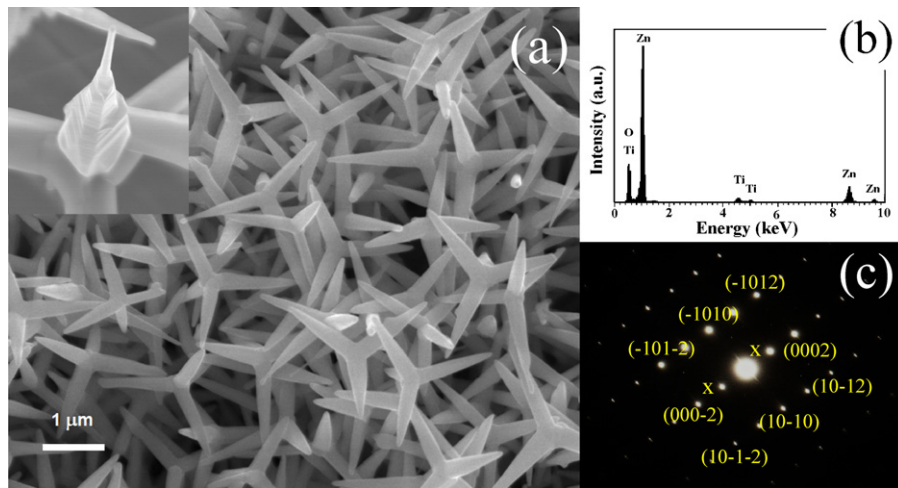


Fig. 2. (a) FE-SEM micrographs with the inset of tetrapod tip with high magnification of the T-TiZnO, (b) EDS spectrum showing Zn, Ti and O signals, and (c) SAED pattern of the T-TiZnO.

also supported with the XRD, EDS, and SAED results and is in good agreement with previous reports [24,28].

From the EDS and SAED results, it is quite difficult to directly confirm that Ti is incorporated into ZnO. However, we can indirectly confirm from energy band gap measurement. We have previously reported that the T-TiZnO exhibited higher energy band gap than that of the T-ZnO [29]. With the result of higher energy band gap from the same hexagonal structure of both the T-TiZnO and T-ZnO, this would suggest that Ti is incorporated into ZnO.

3.2. Ethanol sensing properties

The ethanol sensing characteristic measurement was similar to Ref. [18]. T-ZnO was also synthesized, fabricated as a sensor (called T-ZnO sensor), and tested under the same conditions for comparison with the T-TiZnO and Au/T-TiZnO sensors. In order to investigate the contact property of the sensor, the *I*–*V* characteristics of the T-ZnO sensor was tested at 300 °C in air with applied voltage of –10 to 10 V. It exhibited a linear relation between current and applied voltage indicating an ohmic-contact property.

Fig. 3 shows three cycles of a resistance-temperature response of the Au/T-TiZnO sensor, tested under the ethanol concentration of 50 ppm at 320 °C. The sensor resistance was high in air, but dropped sharply as ethanol vapor was introduced, reaching a nearly saturation state in a few seconds. When the ethanol vapor was reduced

after expose for 120 s, the sensor resistance increased and finally recovered the initial value. The excellent stability and full recovery to an initial value of the sensor signal were clearly seen in this plot.

The plot of the sensor response versus the operating temperature of all sensors under the ethanol concentration of 50 ppm was shown in Fig. 4(a); while, the sensor response exposed under 1000 ppm was shown in Fig. 4(b). It is clearly observed that the sensor response of the Au/T-TiZnO sensor was higher than that of the T-TiZnO and T-ZnO sensors. However, the sensor response of

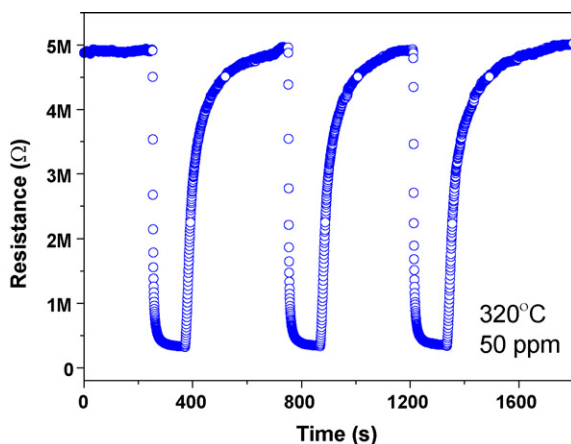


Fig. 3. Three cycles of the resistance-temperature response of the Au/T-TiZnO sensor tested under the ethanol concentration of 50 ppm at 320 °C.

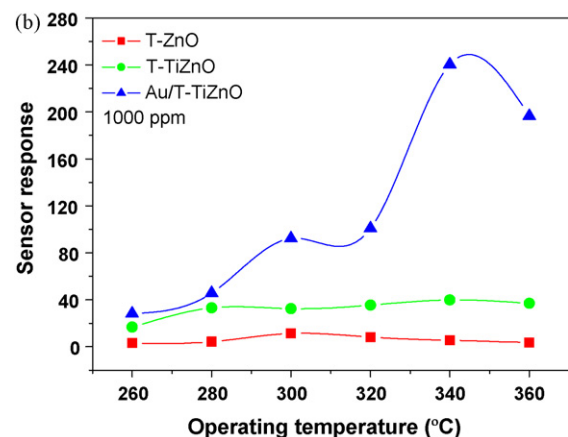
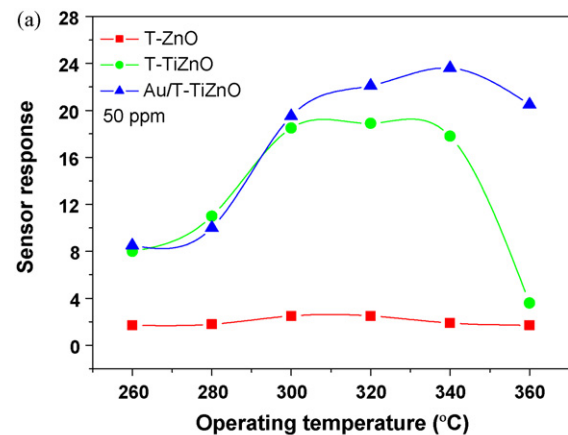


Fig. 4. Sensor response versus the operating temperature of all sensors under the ethanol concentration of (a) 50 ppm and (b) 1000 ppm.

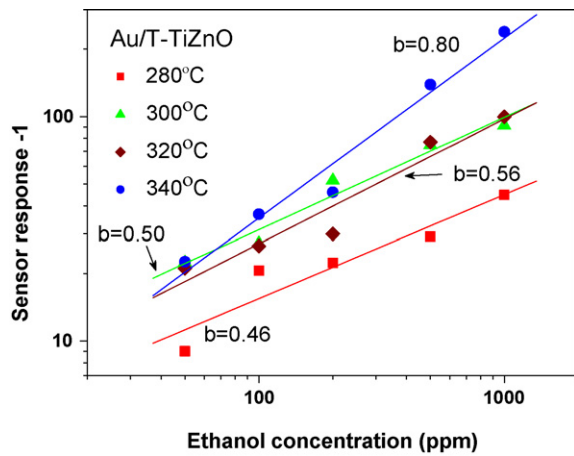


Fig. 5. Plot of $\log(S - 1)$ versus $\log C$ for the Au/T-TiZnO sensor operated at 280, 300, 320, and 340 °C.

the Au/T-TiZnO and T-TiZnO sensors under 50 ppm was similar at the operating temperature of 280–300 °C. But, the Au/T-TiZnO sensor showed a significant improvement in the sensor response at temperatures above approximately 300 °C.

Exposing to the ethanol concentration of 1000 ppm, the more remarkable sensing response of the Au/T-TiZnO sensor was observed. The sensor response of the Au/T-TiZnO sensor is seen to slowly increase, starting from 28 at the operating temperature of 260 °C and reaching about 92 at the operating temperature of 300 °C. Then, it increased more rapidly to about 240 as the operating temperature reached an optimum value of 340 °C. This is about 6 and 23 times higher than the optimum temperature of the T-TiZnO and T-ZnO sensors being 340 and 300 °C, respectively. Furthermore, at the optimum temperature the Au/T-TiZnO sensor exhibited the highest sensor response while the T-TiZnO sensor exhibited higher sensor response than that of the T-ZnO sensor.

Compared with the previous reports, it is worth noting that our ethanol sensor response is higher than that of ZnO nanowires both with and without Pd adsorption [20], flowerlike ZnO nanostructures [30], Ru-doped ZnO nanopowder [22], Al-doped ZnO nanomaterials [23], and also ZnO nanowires [31] even though the size of our sensor material is larger than those of previous reports. However, for sensors based on ZnO nanostructures having diameter less than 15 nm [7,32], our sensor exhibited lower sensor response.

Generally, the sensor response of the metal-oxide semiconductor can be written in a compact form $S = aC^b + 1$ [33], where C is gas concentration, a is a constant depending on type of test gas; sensor material; and operating temperature. In general, b is equal to 0.5 or 1 for adsorbed oxygen species of O^{2-} or O^- , respectively. These adsorbed oxygen species play an important role on surface charge concentration [34,35]. By plotting $\log(S - 1)$ versus $\log C$, the b value can be found from the slope of this plot.

The plot of $\log(S - 1)$ versus $\log C$ for the Au/T-TiZnO sensor operated at 280, 300, 320, and 340 °C was shown in Fig. 5. It should be noted that the b value increased with increase of the operating temperature. At 280 °C, the b value was slightly lower than 0.5. When the sensor was operated at 300 °C, the b value was 0.5 and reached 0.56 as the operating temperature increasing up to 320 °C. The b value at 340 °C was calculated to be 0.80. The deviation from a value of 0.5 may be due to the Au coating effect at higher temperature on the oxygen adsorption species at the surface.

3.3. Explanation of enhancement of the sensor response

In order to explain the enhancement of the sensor response, we have considered the sensor response formula that has been recently

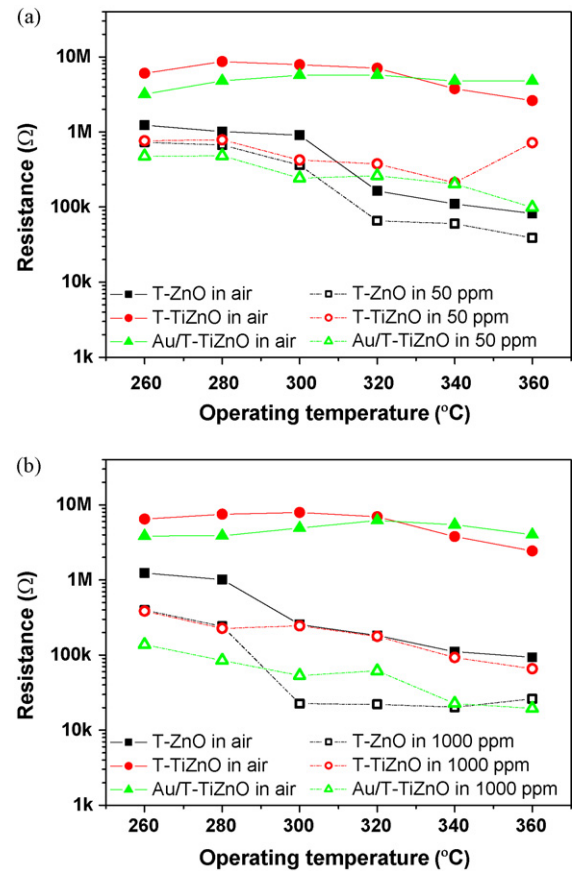


Fig. 6. Sensor resistance versus the operating temperature for all sensors in air and under ethanol concentration of (a) 50 ppm and (b) 1000 ppm.

reported in general form for explaining the sensors based on ZnO [33]. The sensor response formula can be written as

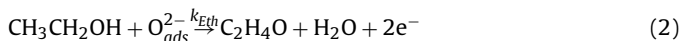
$$S = \frac{R_{air}}{R_{gas}} = \frac{\Gamma_t k_{Eth}(T) [O_{ads}^{ion}]^b}{n_0} C_g^b + 1 \quad (1)$$

where Γ_t is proportional constant, $k_{Eth}(T)$ is a reaction rate constant between adsorbed oxygen species and the ethanol vapor that depends on the operating temperature, O_{ads}^{ion} is adsorbed oxygen species concentration, C_g^b is the ethanol concentration, and n_0 is electron concentration of sensor in air. It should be noted that the term $\Gamma_t k_{Eth}(T) [O_{ads}^{ion}]^b / n_0$ can be regarded as the constant a , with the ethanol concentration, and can be reduced to compact form of $S = aC^b + 1$ as discussed earlier.

The enhancement of the sensor response is due to two reasons: TiO_2 mixing and Au coating. Firstly, the T-TiZnO sensor exhibited higher sensor response than that of the T-ZnO sensor. This can be explained in term of the electron concentration of sensor in air, n_0 . Mixing TiO_2 in ZnO resulted in widening the band gap as demonstrated in our previous work [29]. Thus, n_0 of the T-TiZnO sensor is less than that of the T-ZnO sensor. As seen in the formula, n_0 is inversely proportional to the sensor response. The higher sensor response of the T-TiZnO sensor than that of the T-ZnO sensor is due to having lower n_0 . The evidence for having lower n_0 can be observed by the sensor resistance in air. It can be seen in Fig. 6 that the sensor resistance in air of the T-TiZnO sensor is higher than that of the T-ZnO sensor indicating lower electron concentration.

Secondly, as found earlier, the Au/T-TiZnO sensor exhibited the highest sensor response. This effect can be explained in term of the reaction rate constant between the adsorbed oxygen species and

the ethanol vapor, k_{Eth} as given in Eq. (2)



It is well-known that Au exhibits an excellent catalytic ability [36,37]. Therefore, Au coating would result in the higher reaction rate constant. Since k_{Eth} is directly proportional to the sensor response, Au coating will give higher sensor response. The evidence for having higher k_{Eth} can be observed by the sensor resistance in the ethanol ambient. It is clearly seen in Fig. 6 that the sensor resistance in the ethanol ambient of the Au/T-TiZnO is lower than that of both the T-TiZnO and T-ZnO sensors, indicating the higher reaction rate constant between the adsorbed oxygen species and the ethanol vapor.

In this study, the Au/T-TiZnO sensor has both TiO₂ mixing and Au coating effects which both contribute to the Au/T-TiZnO sensor having the highest sensor response compared with both of the T-TiZnO and T-ZnO sensors.

4. Conclusions

Ethanol sensors have been fabricated based on the T-ZnO, T-TiZnO, and Au/T-TiZnO. The enhancement of the sensor response based on the T-ZnO by TiO₂ mixing and Au coating was observed and can be explained by both the alloying effect and metal catalytic effect, respectively. Moreover, the response enhancement can be empirically explained by using the sensor response formula of ZnO sensor in terms of the electron concentration, n_0 in air and the reaction rate constant, k_{Eth} . TiO₂ mixing resulted in alloying with the T-ZnO, widening the band gap and lowering n_0 , but Au coating resulted in higher k_{Eth} . Lower n_0 and higher k_{Eth} in the sensor response formula gave the higher sensor response. The evidence for both effects can be found in the higher sensor resistance in air and the lower sensor resistance in the ethanol ambient. These techniques for enhancement of the sensor response can be simply explored for other sensing materials such as SnO₂, and TiO₂.

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