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Optical Gas Sensor based on Al-doped ZnO/ZnTPP hybrid thin film

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Abstract. Hybrid optical gas sensors based on Al-doped ZnO/Zinc porphyrin (AZO/ZnTPP) thin films have been fabricated and demonstrated to detect ethanol vapor. Double-sensing layer of AZO and ZnTPP films were deposited on a cleaned glass substrate by RF magnetron sputtering and spin-coating techniques, respectively. We have investigated the influences of Al-doping concentration (0%, 2% and 3 wt% Al₂O₃) on ZnO structure with regarding to enhancing optical gas sensing properties when exposed the films to the volatile. Structural, electrical and optical properties of the AZO thin films were characterized and related to the optical gas sensing responses. It was found that an increase of Al-doped concentration in ZnO structure can also induce a potentially optical sensing response. These results were mentioned that an enhancement of carrier concentration due to Al³⁺ substitution in Zn²⁺ on ZnO structure can generate the adsorbed oxygen ion on the AZO surface as well. Absorption spectra of AZO thin films showed blue shift in near UV region due to releasing of electrons when the adsorbed oxygen ions were interacted with ethanol molecules. According to the introduced the AZO layer to form AZO/ZnTPP sensing film, the results could be demonstrated significantly enhanced the optical responses to the ethanol in broaden range of near UV-visible region at room temperature. Finally, the authors have suggest that the A3ZO/ZnTPP thin film exhibiting a good performance to detect ethanol vapor and overcome a conventional ZnTPP, ZnO/ZnTPP and A2ZO/ZnTPP thin films may be promoted as one of the optical gas sensor in an optoelectronic nose system due to broaden responses at room temperature.

1. Introduction

Metalloporphyrin is a macrocyclic organic molecule which has been introduced to several applications in an optoelectronics due to containing π -conjugated system and high thermal and photo-chemical stabilities [1]. A metal atom located at a centre of porphyrin ring was mentioned as a potential active site to interact with volatile molecules; therefore the electron charges can transfer between the metal atom and the volatile molecule resulting in changes of charge density and optical properties in the porphyrin ring. In the field of gas sensors, zinc porphyrin is one of optical sensing materials being active in a visible light and can present the change of absorption spectrum upon exposure to the volatile organic compounds (VOCs). The UV-visible absorption peaks of ZnTPP normally show



intense absorption at around 400 nm (B-band or Soret band) and two weaker absorption at higher wavelength around 450-700 nm (Q-band) [2-3]; hence, working area of optical sensing properties can also potentially respond to the VOCs in these regions. In order to improve optical sensing region of sensing materials, the researchers have tried to search a hybrid materials with combining active spectrum to cover in other regions. For example, S. Kladsomboon et al. modified ZnTPP/ZnTTBPc/MnTPPCl hybrid thin film based on spin-coating method for alcohol detection. The results of optical sensing response to the vapors have been showed that the data set of sensing signals was improved by covering a whole near UV-visible region (300-800 nm) [4]. Consequently, it was benefit to processing the data via pattern recognition when the modified sensor was used in optoelectronic nose applications which require broaden sensing responses.

Zinc oxide (ZnO) is a well-known gas sensing material for applying in resistive semiconductor gas sensor. According to transparent film, the ZnO thin film is not interested to adopt on optical chemical sensing application in range of visible region; however, its absorption spectrum is well-known as presented in range of UV region as reported in elsewhere [5-7]. For this worth reason, we have expected the effective sensing signals in both of visible and UV regions due to combination of ZnO and ZnTPP (ZnO/ZnTPP) functions, respectively. In the previous studies, the researchers proposed the possible method to improve electrical properties of metal oxide (MOX) based on gas sensors by including doping MOX with a metal. S. M. Chou [8] and R.Dhahri [9] research groups adopted Al-doped ZnO sensing material in resistive gas sensor to detect ethanol vapor and CO gas, respectively. Effect of Al-doping in ZnO was clearly investigated regarding improving of electrical properties due to increasing of carrier concentration. According this result, the electrical conductivity of Al-doped ZnO thin film is greater than pristine ZnO, moreover the present of Al element can produce significant effect on sensing properties due to decreasing of grain size resulting in high surface area as well as aspect ratio [6,10-12]. However almost no one studies the optical gas sensing properties of AZO thin film under UV-visible absorption regions. According to literature review, we found only one previous work that investigated the spectral changes in the transmission properties of ZnO layer due to the effect of the various gases such as ammonia, hydrogen and nitrogen dioxide [13]. For the mechanism of optical gas sensor based on metal oxide materials, it is mentioned about a change in charge density on the surface and a shift of the Fermi level due to adsorption of oxidative and reductive gases [13-15].

In this work, we have combined optical capability of ZnTPP and AZO films to improve sensing properties on broaden sensing wavelength in range of near UV to visible absorption. The effect of Al-doped concentration (0% wt, 2% wt and 3%wt of Al_2O_3) on ZnO structure was also investigated regarding influence to optical sensing properties.

2. Experimental details

2.1 ZnO and Al-doped ZnO films preparations

In this work, ZnO and Al-doped ZnO (AZO) films were prepared by RF magnetron sputtering technique on glass substrates at substrate temperature of 300°C. Home-made ZnO, 2 wt.% Al-doped ZnO (A2ZO) and 3 wt.% Al-doped ZnO (A3ZO) sputtering targets, with the diameter of about 74 millimeters, were prepared from mixed powder of ZnO (99.7%) and Al_2O_3 (99.99%) powders sintered at 1300° for 3 hours in air. Before films deposition, the glass substrates were cleaned by immersion in nitric acid for many hours to remove organic materials on the surface. After that they were ultrasonically cleaned by steeping in detergent and ethanol for 10 minutes each and the blow dry with compressed air. The glass substrates were then put into vacuum chamber with fixed target-substrate spacing of 60 millimeters. The vacuum chamber was evacuated to background pressure less than 5.0×10^{-3} mbar before high purity argon (99.995%) gas was then flow into the vacuum chamber up to 5.0×10^{-3} mbar and the films were deposited at RF power of 150 W for 35 minutes. After film depositions,

they were characterized crystal structure, electrical and optical properties by X-ray diffraction, Hall measurement and UV-Vis-NIR spectrometry respectively.

2.2 ZnTPP, ZnO/ZnTPP and AZO/ZnTPP thin films preparations

After the ZnO, A2ZO and A3ZO films were performed on an individual clean glass substrate at the first layer within the area of $2.5 \times 2.5 \text{ cm}^2$, ZnTPP thin film was simply carried on by spin-coating process at the upper layer. 5, 10, 15, 20-Tetraphenyl-21H, 23H-porphine zinc was purchased from Sigma-Aldrich and its solution was prepared by dissolving 5 mg of the solid in 1 ml of chloroform. 40 μl of the ZnTPP solution was dropped on as-prepared individual metal oxide thin films and then spreading over with 1,000 rpm for 30 s. After that, the specimens were heated in an air oven at 80°C for 1 hour. A single layer of ZnTPP film on a cleaned glass substrate was also prepared in order to compare the sensing properties regarding to working of the hybrid thin films.

2.3 Optical sensing Characterization

Due to sensing ability to alcohol vapors of ZnTPP thin film proposed in the previous work [16]; hence in this work, we have intended to demonstrate these optical sensing films to ethanol vapor. The optical thin films were put into a stable ethanol atmosphere chamber at room temperature [17]. The gas sensing capability have been investigated in term of change of optical absorption spectra of the films by using a UV-VIS spectrometer (Biochrom, Libra S70) with scanning wavelength from 250 to 800 nm. Sensing responses were calculated from variation in area under curve of the absorption spectra when the film was in ethanol atmosphere with respect to an ambient air. Integral of each spectrum region can be simply extracted using trapezoidal approximation. The absorption spectra of the ZnO/ZnTPP and AZO/ZnTPP hybrid thin films were divided into four regions (R1: 300–370, R2: 400–440, R3: 440–520, R4: 520–640 nm) based on the optical response to ethanol. A single layer of the ZnTPP thin film was observed the optical response in R3-R4 region whereas the metal oxide (ZnO, A2ZO and A3ZO) thin films were measured only in R1 region. The optical sensing response upon responses with ethanol was defined as following equation:

$$\% \text{ Response to EtOH} = \frac{A_{\text{EtOH}} - A_{\text{Air}}}{A_{\text{Air}}} \times 100 \quad (1)$$

where A_{EtOH} and A_{Air} is the integral of the absorption spectrum in an interested wavelength region measured under ethanol atmosphere and ambient air, respectively.

3. Results and discussion

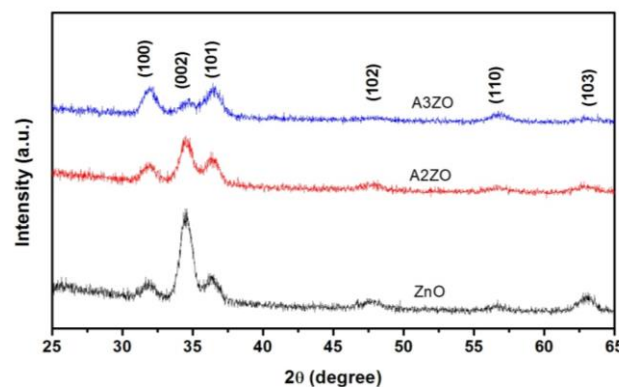


Figure 1. XRD spectra of AZO thin film at different Al-dopant concentrations prepared at substrate temperature of 350°C .

XRD pattern of ZnO and Al-doped ZnO thin films are depicted in Figure 1. Diffraction peaks of the deposited films exhibit polycrystalline structure containing a strong preferred orientation along the (200) plane (c-axis) and including other weak orientation in (100), (101), (102), (110) and (103) planes. It can be noticed that doping with 2 wt% Al_2O_3 leads to decrease of the (002) peak while (101) and (110) peaks become higher; furthermore, the (002) peak seem disappear when Al doped up to 3 wt%. These results are in accordance with the previous reports which mentioned that increase of Al-doping concentration in the ZnO structure leads to a random orientation [18-19].

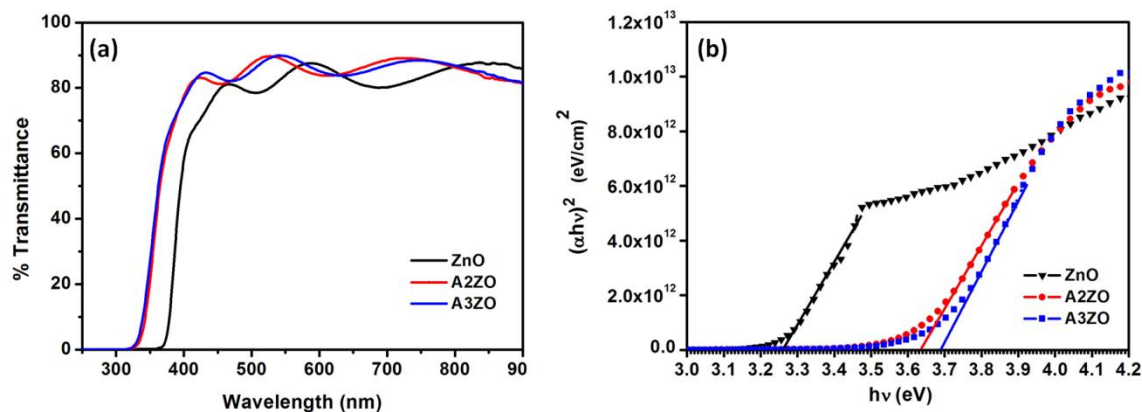


Figure 2. (a) Optical transmission spectra and (b) optical band gap of Al-doped ZnO deposited films.

Table 1. The calculated electrical properties of ZnO and Al-doped ZnO thin film.

Thin films	Carrier concentration ($\times 10^{21} \text{ cm}^{-3}$)	Mobility ($\text{cm}^2 / \text{V} \cdot \text{s}$)	Resistivity ($\times 10^{-3} \Omega \cdot \text{cm}$)	Optical band gap (eV)
ZnO	0.048	11	34.5	3.27
A2ZO	1.24	9	1.66	3.64
A3ZO	1.56	8	1.49	3.68

Optical transmittance spectra were measured through UV-Visible-NIR spectrophotometer in wavelength range of 250-2500 nm as shown in Figure 2(a). From the results, it was observed that all of the films show a transmittance more than 80% in visible wavelength region and the sharp absorption edges were blue shift with an increase of Al doping concentration. The shifted absorption edges are strongly correlated with the optical energy gap which can be estimated by extrapolating the linear portion of the Tauc's plot to photon energy axis (x-axis) as shown in Figure 2(b) and reported in Table 1. The blue shift in the optical band gap of the AZO thin films can be explained corresponding to Burstein-Moss shift (BM shift) as reported by other authors [10-11,20-21]. Al^{3+} substitution in Zn^{2+} on the ZnO structure will leave one electron as a free electron ($\text{Al}^{2+} \longrightarrow \text{Al}^{3+} + e^-$) leading to occupying the lower energy state at the bottom of the conduction band and resulting in moving the Fermi level up into the conduction band. As a result; larger energy gap is obtained for Al doped ZnO thin films. From the results of the Tauc's plot the optical band gap presented with 3.27 eV up to 3.64 eV and 3.70 eV regarding to increasing of Al doping concentration. Increasing of the carrier concentration caused from Al^{3+} electron donors also enhance conductivity of the AZO films as shown all results in Table 1. It was found that the carrier concentration of ZnO films was $4.80 \times 10^{19} \text{ cm}^{-3}$ and

then increased two order of magnitude to $1.24 \times 10^{21} \text{ cm}^{-3}$ and $1.56 \times 10^{21} \text{ cm}^{-3}$ for 2 wt% and 3 wt% of Al_2O_3 doped ZnO films respectively. Increase of carrier concentration resulted in decrease of electrical resistivity from $3.45 \times 10^{-2} \Omega\cdot\text{cm}$ down to $1.49 \times 10^{-3} \Omega\cdot\text{cm}$ while mobility was almost unchanged.

From these results, it was seem that the change of carrier concentration on the surface of ZnO and Al-doped ZnO film can affect to the energy-band structure; and, therefore, the Al-doped ZnO can improve gas sensing performance. The enhancement of the responses in the chemo-electrical gas sensors due to this effect was reported by several research groups [11,20]. However, almost no one mentioned about applying these thin films on the optical gas sensors under UV-visible absorption. In this work, we have added the ZnO or Al-doped ZnO sensing layer at the bottom of ZnTPP thin film to observe the optical sensing response to ethanol vapor at room temperature.

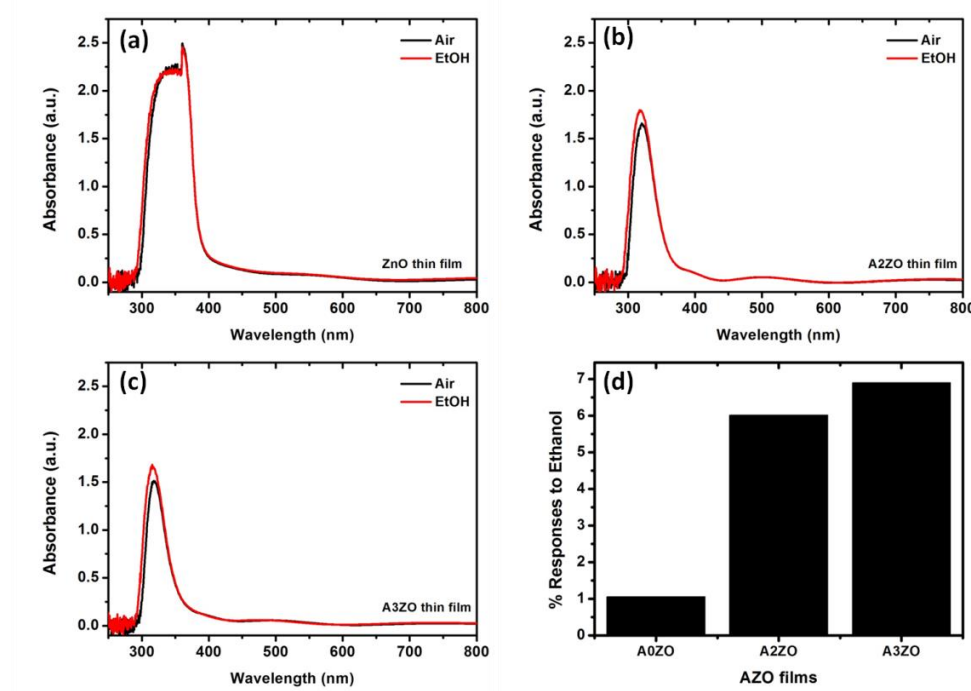


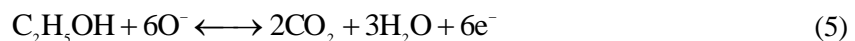
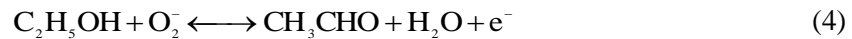
Figure 3. (a) Comparing the absorbance spectra of (a) the ZnO, (b) the A2ZO, (c) the A3ZO films upon exposure to ambient air and ethanol vapor at room temperature (d) the calculated optical sensing responses to ethanol vapor of the (a), (b) and (c) films within the wavelength range of 300 to 370 nm.

Figure 3(a), Figure 3(b) and Figure 3(c) show the optical absorption spectra of the ZnO, A2ZO and A3ZO thin films, respectively, in ambient air comparing with that exposed in ethanol vapor. The sensing responses of all thin films show solvent effect with shifting of absorption spectra to a shorter wavelength (blue-shift) when the films were exposed with ethanol vapor which may be ascribed as followed.

Upon exposing the ZnO and Al-doped ZnO films to the ambient air, oxygen gas will adsorb on the film surface and capture free electron from the conduction band resulting in forming of O_2^- or O^- ions, following the given equations [22]:



In addition, increasing of the carrier concentration on the surface with increasing of Al-doped concentration may induce higher O_2 chemisorbed on the surface of the films. When the films was exposed by ethanol vapor, the adsorbed oxygen ion species reacts with the ethanol molecule and leaves electron back to the conduction band of the ZnO and AZO films. Enlargement of these free electrons result in an increase of optical band gap which we recall as Burstein–Moss shift as mentioned in above. The oxidation reactions of ethanol on the surface may take place as follows:



In this work, we have suggested that both O_2^- and O^- ions might be generated on the AZO surface therefore the oxidation reactions in Equation (4) and Equation (5) were possibly occurred. Various oxygen ion species adsorbed on the metal oxide surface were reported that they could be formed depending on temperature, forming O_2^- (<100 °C), O^- (100-300 °C), or O^{2-} (>300 °C) [22]. Based on operating at room temperature, Equation (2) and Equation (4) are often picked up to explain the sensing mechanism of the metal oxide materials.

In addition, many authors [6,10-12] reported that enhancement of the surface-to-volume ratio as well as increase of concentration of lattice oxygen vacancies was given as one of the reasons to promote more adsorption of oxygen on the metal oxide surface which, therefore, Equation (3) and Equation (5) are possible. These mentions were reported in the previous work [23]. We additionally suggest previously that an influence of Al-doping on ZnO structure also contribute to the higher adsorption of oxygen due to increasing of carrier concentration. Besides these effects, there was advantage of measuring UV absorption which contributes to increase the density of adsorbed oxygen ion species. In the previous reports, UV illumination was used to activate for enhancement of electrical gas sensing based on Al-dope ZnO [9] and Cu-dope ZnO [24] sensors and the results could show improvement of responses obviously. Figure 3(d) represents the sensing response which extracted from a change of area under a curve in R1 region of absorption spectrum presented in Figure 3(a). The results show improvement of sensing response clearly when exposed to ethanol vapor according with increasing of Al-doping concentration.

Figure 4(a) and Figure 4(b) show the optical absorption spectra of the ZnTPP and the A3ZO/ZnTPP thin films in ambient air comparing with that in ethanol vapor atmosphere, respectively. In the Figure 4(a), the results are observed that the optical absorption spectrum is dominated by the intend absorption Soret band located at 434.5 nm and two weak adsorption Q band located around 520-640 nm, which have been arised from the corresponding π - π^* transitions. Due to the interaction of ethanol on ZnTPP surface, the Soret band shows a slight shift from 434.5 nm to 435.5 nm which indicated as a red shift. Sensing mechanism between analyst and ZnTPP surface was explained that it involve partial charge transfer from ethanol molecules to porphyrin ring resulting in enhancement of the density in the electronic levels available in π - π^* transitions. The worth evident of charge transfer was reported by the molecular simulation [16,25] that alcohol molecules could adsorb on the ZnTPP molecule and transfer charge to the alpha, beta and meso positions of the porphyrin structure via interaction at the central metal atom. In addition, these results are also in accordance with the previous report which showed a red shift of absorption spectra when the ZnTPP film based on spin-coating film interacted to methanol vapor [26].

In the Figure 4(b), the absorption spectrum of the A3ZO/ZnTPP thin film was picked up to represent the combination of ZnO or Al-doped ZnO with ZnTPP thin films. The result shows contribution of the AZO and the ZnTPP absorption spectra which a strong peak of AZO locates at 318 nm and the Soret band and Q-band of ZnTPP present at 435.5 nm and around 520-640 nm, respectively. Sensing responses in each region to ethanol vapor were determined and demonstrated for the ZnTPP and the hybrid thin films as shown in Figure 4(c).

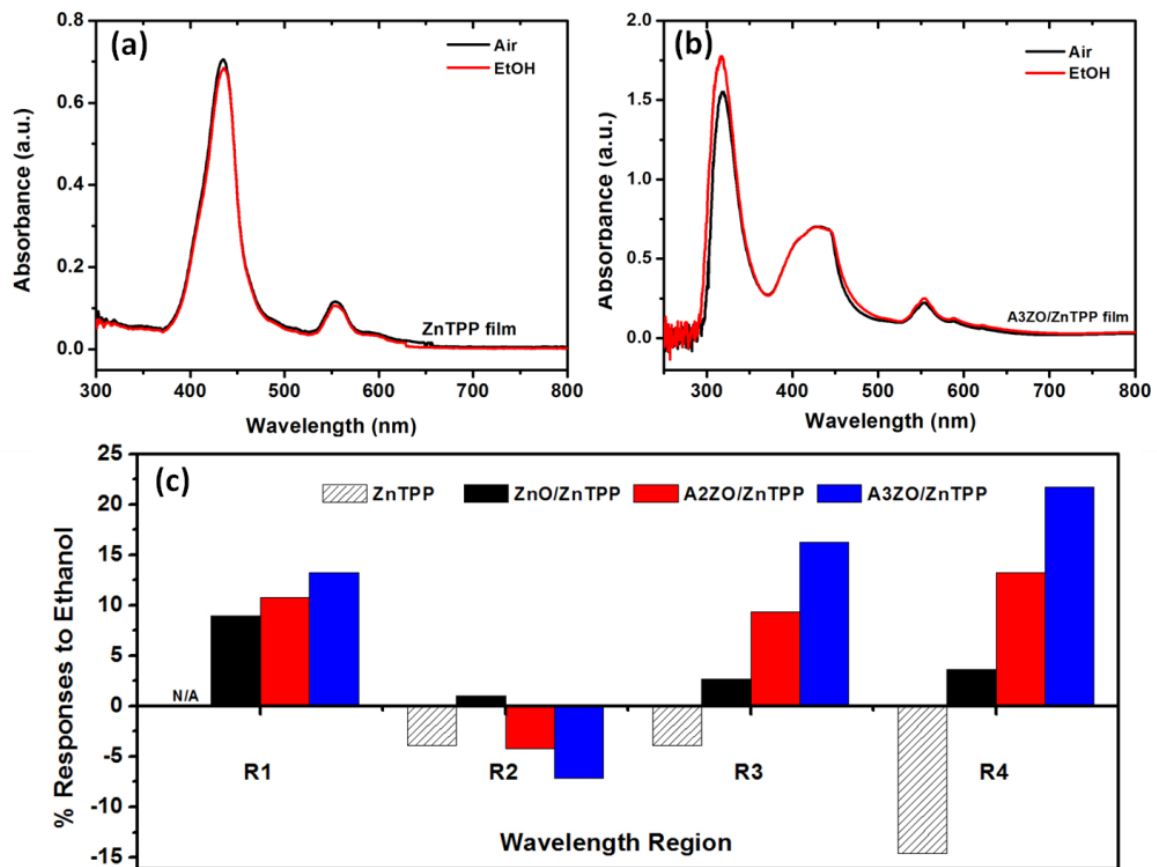


Figure 4. Comparing the absorbance spectra of (a) the ZnTPP, (b) the A3ZO/ZnTPP films upon exposure to ambient air and ethanol vapor at room temperature (c) the calculated optical sensing responses to ethanol vapor of the ZnTPP, the ZnO and the Al-doped ZnO thin films by observing at various wavelength regions

According to the results, it seems that the Al-doping concentration can enhance the optical sensing response; not only R1 region but also in the R2, R3 and R4 regions. Moreover the hybrid thin films can improve the optical responses in R2-R4 compared with a conventional ZnTPP thin film.

4. Conclusions

The AZO/ZnTPP thin films were fabricated and characterized for their optical gas sensing properties based on observing UV-visible absorption at room temperature to detect ethanol volatile comparing with the conventional ZnTPP thin film. Effect of the contributed Al on ZnO was discussed that it was resulting in an increasing of carrier concentration as well as improvement of energy gap and corresponding to the improvement of ethanol sensing responses. In UV-visible absorption spectra, we could observe blue shift based on Burstein–Moss shift effect due to increasing of Al-dopant and interacting with ethanol which the both effects causes of increasing electron on conduction band. The experimental results showed clearly enhancement of sensing signals for AZO/ZnTPP and can overcome the conventional sensing film. In this work, the A3ZO/ZnTPP thin film presented the best performance and showed sensing responses in broaden range; hence in the nearly future we would like to promote this film as one of the sensing film in an optoelectronic nose system which required broaden response and operating at room temperature.

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References

- [1] Suslick K S, Rakow N A, Kosal M E and Chou J H 2000 *Journal of Porphyrins and Phthalocyanines* **4** 407
- [2] Chandra R, Tiwari M, Kaur P, Sharma M, Jain R and Dass S 2000 *Indian Journal of Clinical Biochemistry* **15** 183
- [3] Spadavecchia J, Rella R, Siciliano P, Manera M G, Alimelli A, Paolesse R, Natale C D and D'Amico A 2006 *Sensors and Actuators B: Chemical* **115** 12
- [4] Kerdcharoen T and Kladsomboon S 2013 *Applications of nanomaterials in sensors and diagnostics* vol 14, ed A Tuantranont (Berlin, Heidelberg:Springer) p 237
- [5] Zheng Z Q, Yao J D, Wang B and Yang G W 2015 *Scientific Reports* 11070 (2015)
- [6] Jun M C, Park S U and Koh J H 2012 *Nanoscale Research Letters* 7:639
- [7] Dinh D A, Hui K N, Hui K S, Singh J and Kuma P 2013 *Reviews in Advanced Sciences and Engineering* **2** 259
- [8] Chou S M, Teoh L G, Lai W H, Su Y H and Hon M H 2006 *Sensors* **6** 1420
- [9] Dhahri R, Hjiri M, Mir L E, Bonavita A, Iannazzo D, Latino M, Donato N, Leonardi S G and Neri G 2016 *Journal of Physics D Applied Physics* 49(2016)135502
- [10] Srinatha N, Raghu P, Mahesh H M, Angadi B 2017 *Journal of Alloys and Compounds* **722** 888
- [11] Aydın H, Yakuphanoglu F and Aydın C 2019 *Journal of Alloys and Compounds* **723** 802
- [12] Aprilia A, Fernando H, Bahtiar A, Safriani L and Hidayat R 2018 *Journal of Physics: Conf. Series* 1080 (2018) 012009
- [13] Struk P, Pustelny T, Gołaszewska K, Borysiewicz M A and Piotrowska A 2015 *Bulletin of the Polish Academic of Sciences Technical Sciences* **68** 829
- [14] Zhyrovetsky V M, Popovych D I, Savka S S and Serednytski A S 2017 *Nanoscale Research Letters* 12:132.
- [15] Berger D, Moura A P, Oliveira L H, Bastos W B, Porta F A L, Rosa I L V, Li M S, Tebcherani S M, Longo E and Varela J A 2016 *Ceramics International* **42** 13555
- [16] Kladsomboon S, Lutz M, Pogfay T, Puntheeranurak T, Kerdcharoen T 2012 *Journal of Nanoscience and Nanotechnology* **12** 5240
- [17] Kladsomboon S, Thippakorn C and Seesaard T 2018 *Sensors* **18** 3189
- [18] Mamat M H, Sahdan M Z, Khusaimi Z, Ahmed A Z, Abdullah S and Rusop M 2010 *Optical Materials* **32** 696
- [19] Muiva C M, Sathiaraj T S and Maabong K 2011 *Ceramics International* **37** 555
- [20] Kolhe P S, Shinde A B, Kulkarni S G, Maiti N, Koinkar P M and Sonawane K M 2018 *Journal of Alloys and Compounds* 748(2018)
- [21] Muchuweni E, Sathiaraj T S, Nyakoty H 2017 *Heliyon* 3(2017)e00285
- [22] Lin P, Chen X, Zhang K and Baumgart H 2018 *ECS Journal of Solid State Science and Technology* **7** Q246
- [23] Kumar R A 2015 *Int. Journal of Applied Sciences and Engineering Research* **4** 427
- [24] Peng L, Xie T F, Yang M, Wang P, Xu D, Pang S, Wang D J 2008 *Sensors and Actuators B* **131** 660
- [25] Kladsomboon S and Kerdcharoen T 2012 *Analytica Chimica Acta* **757** 75
- [26] Jing L, Jianhua X and Shuang X 2011 *Energy Procedia* **12** 625