

Contents lists available at [ScienceDirect](http://ScienceDirect.com)

Analytical Chemistry Research

journal homepage: www.elsevier.com/locate/ancr

Gas sensing properties of indium–gallium–zinc–oxide gas sensors in different light intensity

Kuen-Lin Chen^a, Guo-Jhen Jiang^b, Kai-Wei Chang^b, Jan-Han Chen^c, Chiu-Hsien Wu^{a,b,*}^aDepartment of Physics, National Chung Hsing University, Taichung 402, Taiwan^bInstitute of Nanoscience, National Chung Hsing University, Taichung 402, Taiwan^cDepartment of Materials Science and Engineering, Da-Yeh University, Changhua 515, Taiwan

ARTICLE INFO

Article history:

Received 24 December 2014

Revised 27 February 2015

Accepted 2 March 2015

Available online 10 March 2015

Keywords:

Gas sensor

Gas sensitivity

Light intensity

ABSTRACT

We have successfully observed the change in indium–gallium–zinc–oxide (IGZO) gas sensor sensitivity by controlling the light emitting diode (LED) power under the same gas concentrations. The light intensity dependence of sensor properties is discussed. Different LED intensities obviously affected the gas sensor sensitivity, which decays with increasing LED intensity. High LED intensity decreases not only gas sensor sensitivity but also the response time (T_{90}), response time constant (τ_{res}) and the absorption rate per second. Low intensity irradiated to sensor causes high sensitivity, but it needs larger response time. Similar results were also observed in other kinds of materials such as TiO_2 . According to the results, the sensing properties of gas sensors can be modulated by controlling the light intensity.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Gas sensing is receiving increasing attention in industrial production, medical applications, and environmental monitoring [1–5]. A gas sensor's good performance is indicated by factors such as sensitivity, response time, energy consumption, long term monitoring, and reproducibility [4]. To achieve good gas sensing performance, several methods [6] (optical, gas chromatographic, and acoustic methods) and materials (metal oxide semiconductors [3], carbon nanotubes [7], and polymers [8]) have been developed.

Metal oxide semiconductors (MOS) are the most common sensing materials. The advantages of MOS are their low cost, fast response, wide range of target gases, and long lifetimes. However, they also have the disadvantages of high energy consumption and low selectivity. To enhance the sensitivity of MOS sensors, the sensors have typically been heated to high temperatures (200–500 °C) [9–11]; however, this strategy is inconvenient for long-term operation. The recent progress in light emitting diode (LED) technology has enabled the production of different wavelengths and powers of LEDs [12]. Also, this development has enabled a wide usage and study of LEDs in gas sensors. Ultraviolet (UV) light irradiation has been proposed for operating some metal oxide gas sensors at room temperature [13–15]. Our

previous experimental results suggest that continuous UV irradiation by a single UV LED can replace conventional heating, and UV lamps to enhance the sensing properties of SnO_2 gas sensors [16]. However, a detailed experiment about the relation between LED power (intensity) and gas sensor sensitivity is still lacking. In this study, indium–gallium–zinc–oxide (IGZO) film sensors were irradiated with different LED intensities under ozone environment [11,17–19]. The sensitivity, response time, and time constant of the sensors irradiated by different LED power are discussed.

2. Experimental

N-type transparent IGZO Thin films with thicknesses of 60–70-nm were deposited on 5 mm × 5 mm glass substrates using an RF-sputtering system with an IGZO ceramic target (atomic ratio In:Ga:Zn = 1:1:1) [11,20,21]. During the sputtering process, a 200-mtorr pure argon atmosphere was maintained, and the substrate was maintained at room temperature (25 °C). X-ray diffraction analysis revealed that the IGZO film was amorphous in nature. No crystalline peaks appear in the XRD pattern of any of the films deposited at temperatures up to 600 °C. Thus, IGZO film deposited below 600 °C reveals amorphous [20].

The amorphous IGZO (a-IGZO) films were placed in a home-made chamber with dimensions of 13.0 cm × 6.5 cm × 5.5 cm. The thin films were continuously irradiated using a 370-nm UV LED at room temperature (25 °C). The LED power follows $P = I_{app} \times V$, where P , I_{app} , and V are LED power, applied current, and voltage, respectively. Thus, LED power can be modulated by

* Corresponding author at: Department of Physics, National Chung Hsing University, 250 Kuo Kuang Rd., Taichung 402, Taiwan. Tel.: +886 4 22840427; fax: +886 4 22862534.

E-mail address: chwu@phys.nchu.edu.tw (C.-H. Wu).

the applied current. The distance between the IGZO thin film and the LED is approximately 0.5 cm. The light intensity (I) follows as $I = \frac{P}{A}$, where A is the area. The LED power was measured by a power meter. The intensity depends on light power at a fixed distance between LED and film. Ozone was generated from an ozone generator and passed through a flow meter. The ozone gas was mixed with dry air (RH $\sim 25 \pm 2\%$) from an air pump before channeling it into the homemade test chamber. Ozone was first detected by the thin film sensor, and the O_3 concentration inside the chamber was also monitored using an O_3 monitor (2B Technologies 106-L) [16].

In this work, the film sensor was continuously irradiated with the UV LED. The IGZO films were first exposed to a UV LED at a fixed power. The generation of electron–hole pairs caused the sensor resistance to decrease until a stable state (the lowest resistance) was reached. The resistance increased as a result of adsorption process and reached equilibrium with ozone channeling into the chamber. Subsequently, when the adsorption process reached equilibrium under ozone environment, ozone was turned off, and the LED power was changed. The resistance of the film during cyclic exposure to trace gas concentrations was measured using a multimeter, and the data was collected by a computer using data acquisition software.

3. Results and discussion

Fig. 1 shows the resistance–time (R – T) curve of an IGZO thin film under LED exposure with a constant intensity of 13.93 mW/cm² while maintaining constant O_3 concentrations of 0.5 and 1 ppm. The lowest equilibrium resistance (R_a), resistance change (ΔR), sensitivity ($S = (R_g - R_a)/R_a$), and sensor response time varied slightly with the same LED power (Fig. 1) [11]. The response of the sensor was almost constant for three cycles, demonstrating the good reproducibility of the sensor as well as the good performance of our IGZO films. Fig. 2 shows the rates of ozone desorption under different LED intensities. First, 0.5 ppm of ozone was absorbed by the IGZO film under irradiation at LED intensity of 13.93 mW/cm². The intensity of LED was changed, and the ozone was turned off when saturation resistance was reached, as shown in the top of Fig. 2. The bottom of Fig. 2 shows the R – T curves under different light intensities during the desorption processes. The saturation resistances were almost the same under the same environment (intensity and ozone concentration).

When LED irradiates the film, the following response equations apply.

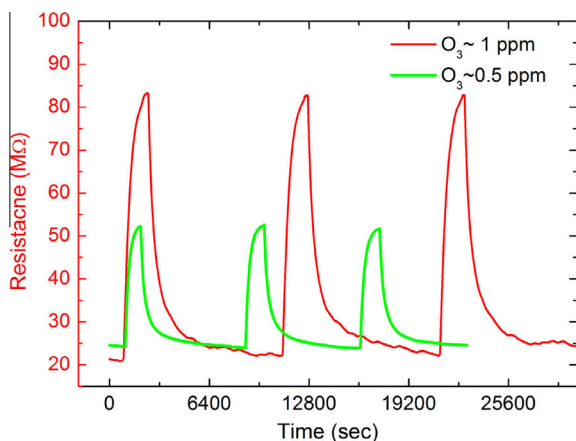
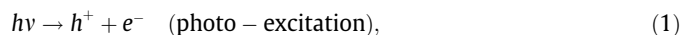
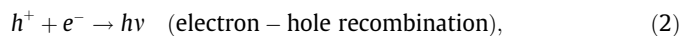
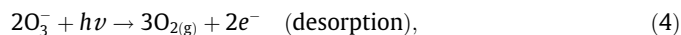


Fig. 1. The resistance–time curves of IGZO sensor at 0.5 and 1 ppm ozone.



When measurements are performed, the following response equations of absorption and desorption apply.



The peaks in the bottom of Fig. 2 were induced by electron–hole combination; at low intensity, the generation of electron–holes was reduced, while the recombination of electron–holes increased (Eqs. (1) and (2)). However, the decreased rate of resistance depends on light intensity after the gas is shut off; greater irradiation intensity resulted in a faster ozone desorption rate (Eqs. (3) and (4)). The R – T curves also revealed that R_a varied with LED power. The lowest resistance decreased as the light intensity increased, which may be explained on the basis of the number of excited molecules. As more intense light irradiates the IGZO molecules, a larger number of molecules get excited, which may generate more electron–hole pairs (Eq. (1)). Thus, the lowest equilibrium resistance was found to decrease with increasing light intensity.

Fig. 3 shows the R – T curves under different LED powers while maintaining a constant O_3 concentration of 2 ppm. The LED intensity was varied from 1.41 to 13.93 mW/cm², as shown by the blue line in Fig. 3. The inset shows the enlarged graph of R – T curve. The lowest resistances are obvious different under different intensities. Fig. 4 shows that sensor's R_a and resistance of sensor in gas (R_g) depend on the light intensity. A larger intensity resulted in a significantly lower R_a and R_g , which both exhibited an exponential response to LED intensity. The $R_g \sim 900$ MΩ was very high under an intensity of 1.41 mW/cm²; however, the change in R_g became small when the intensity was larger than 9.25 mW/cm². The same results were observed in different samples. The results can be explained by the following relationship: $\frac{dn}{dt} = \frac{dN_{\text{abs}}}{dt} - \frac{dN_{\text{des}}}{dt}$, where dn/dt is the net rate of absorption of O_3 molecules, and dN_{abs}/dt and dN_{des}/dt are the rates of absorption and desorption of O_3 molecules, respectively (Eqs. (3) and (4)). The adsorption–desorption activity at any time causes the adsorption–desorption processes to reach equilibrium under continuous irradiation. The resistance of sensor is proportional to $\frac{dn}{dt}$ and resistance will increase when $\frac{dN_{\text{abs}}}{dt} > \frac{dN_{\text{des}}}{dt}$ (ozone channels into test box). It will reach equilibrium if $\frac{dN_{\text{abs}}}{dt} \approx \frac{dN_{\text{des}}}{dt}$, and $\frac{dn}{dt}$ will be negative when the ozone stops channeling into the test box ($\frac{dn}{dt} = 0 - \frac{dN_{\text{des}}}{dt}$). Therefore, the different R_g observed in Fig. 3 is caused by different net desorption rates at the different intensities. R_g will be reduced with the same gas concentrations at high intensity because the rate of desorption (dN_{des}/dt) is increased.

Fig. 5 shows the sensitivity (S) and resistance change ($\Delta R = R_g - R_a$) under different intensities. The sensitivity to ozone gas, $S = (R_g - R_a)/R_a$, is a function of light intensity. The sensor sensitivity is found to decrease with increasing intensity; ΔR and S are approximately 843 MΩ and 13.7, respectively, at 1.42 mW/cm² and approximately 93 MΩ and 8.29, respectively, at 13.92 mW/cm². With increasing intensity and with more electrons released from the trap state into the conduction band, the surface desorption reaction proceeds more actively (Eq. (4)). Different LED powers obviously affected resistance change, which exponentially decays with increasing LED power. No obvious regular tendency is observed for the decay of S in our experiments. The change of resistance is considerably large at low intensity; this large ΔR will be beneficial for detecting stably low gas concentrations.

Fig. 6 shows the response time (T_{90} : R reaches to the 90% of equilibrium value) and response time constant (τ_{res}) under different intensities [11,22]. The R – T curves were fitted by a simple function of the form $R = A - Be^{-t/\tau_{\text{res}}}$, where A and B correspond to

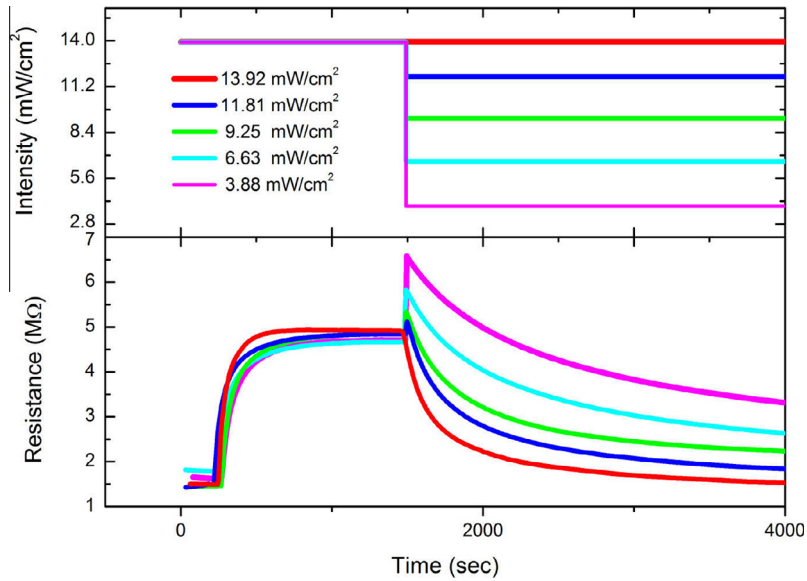


Fig. 2. The rates of ozone desorption under different LED intensities.

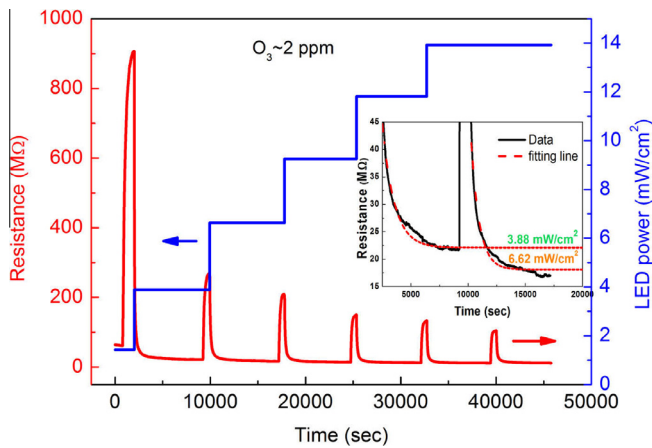


Fig. 3. The R - T curves under different LED powers while maintaining a constant O_3 concentration of 2 ppm.

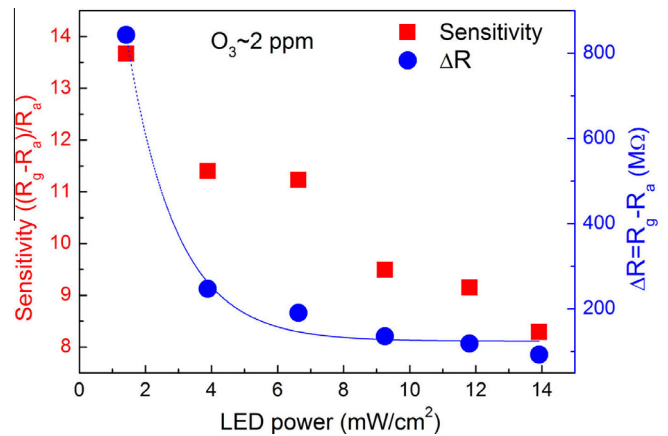


Fig. 5. The sensitivity (S) and resistance change ($\Delta R = R_g - R_a$) of IGZO sensor under different intensities.

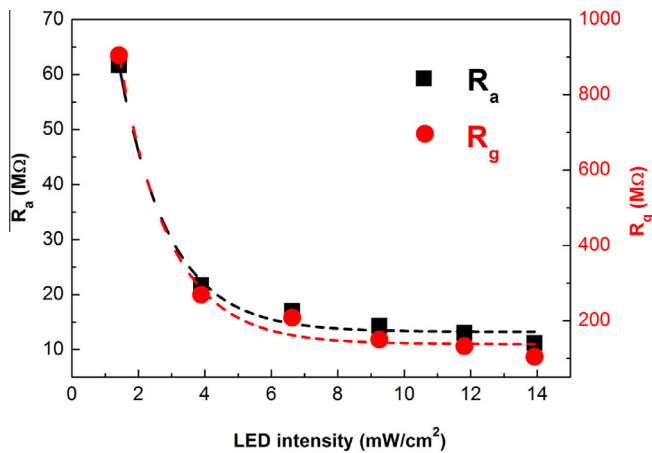


Fig. 4. Sensor's resistances in air and in gas (R_g) depend on the light intensity.

R_g and ΔR . The τ_{res} decreased with increasing intensity; τ decreased from 259.3 to 80.3 s when the intensity increased from

1.42 to 13.92 mW/cm^2 . The results can be fitted with one exponential decay function. A similar decay tendency is observed for T_{90} ; τ decreased from 600 to 205 s when the intensity increased from 1.42 to 13.92 mW/cm^2 . High intensity causes a short response time.

Fig. 7 shows the first-order differential (dR/dt) for the R - T curve of Fig. 3 [23]. It indicates the rate of resistance variation caused by net absorption (the numbers of absorbed molecules minus desorbed ones) of O_3 molecules per second. The curves for different intensities have different raising rates, implying that the rate of change in resistance is also different. The value of dR/dt is positive and dependent on the intensities with the same ozone concentration during absorption. Moreover, different peaks are observed for different intensities in the first-order derivative curves (Fig. 7). At lower intensity, the instantaneous adsorption of ozone molecules is higher, causing a high rate of change. The maximum rate of change of adsorption as a function of intensity is shown in Fig. 8. The relation between the maximum rate of change ($(dR/dt)_{max}$) and light intensity is approximately exponential. These results can also be explained by the competition between adsorption and desorption rates at different intensities.

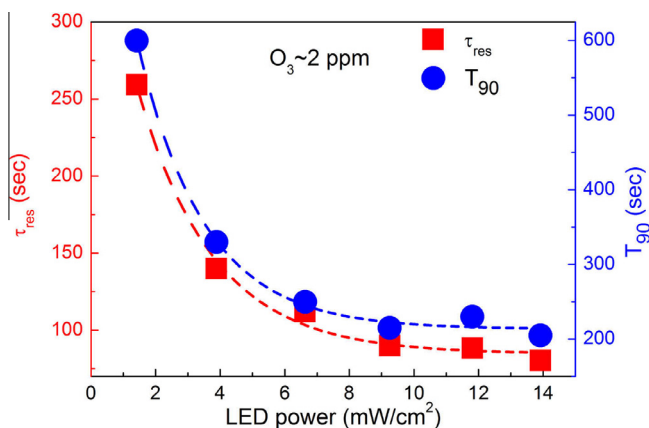


Fig. 6. The response time (T_{90}) and response time constant (τ_{res}) under different intensities.

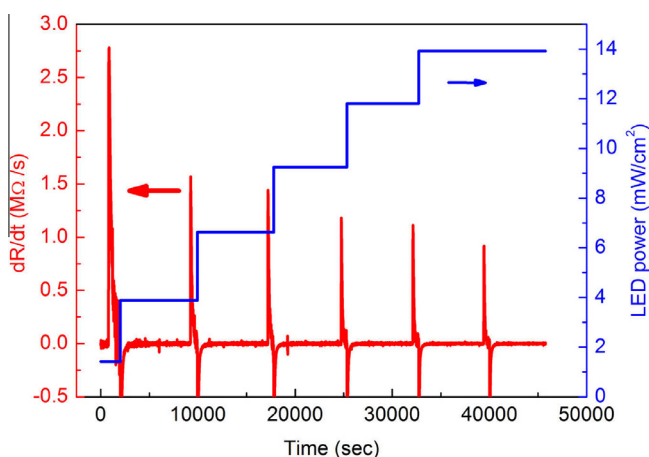


Fig. 7. The first-order difference for the R - T curve of Fig. 3

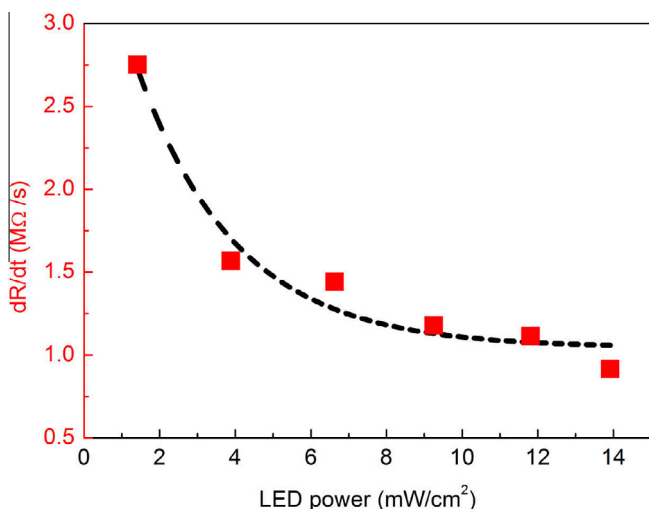


Fig. 8. The maximum rate of change of adsorption as a function of intensity.

Fig. 9 shows the resistance-time curve of an TiO_2 thin film under different LED powers while maintaining a constant O_3 concentration of 1.7 ppm. R_a , R_g and ΔR also depend on the light intensity. The results of TiO_2 film are consistent with those of IGZO film. A larger intensity resulted in a significantly lower R_a and R_g .

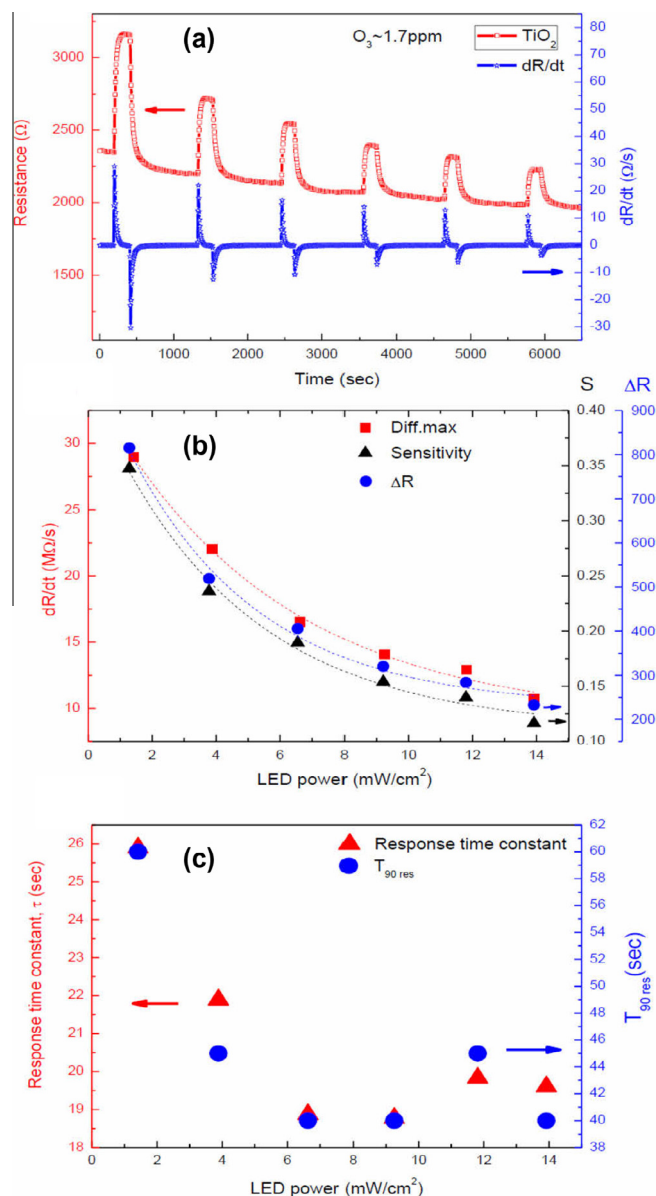


Fig. 9. The sensing properties of TiO_2 sensor at 1.7 ppm ozone under different intensities. (a) The resistance-time curves and first-order difference for the R - T curve. (b) The sensitivity the maximum rate of change of resistance and resistance change of TiO_2 sensor under different intensities. (c) The response time (T_{90}) and response time constant (τ_{res}).

Fig. 9(b) shows the S , ΔR and dR/dt under different intensities. S , ΔR and $(dR/dt)_{max}$ to ozone gas are a function of light intensity, which all exhibited an exponential response to LED intensity. Fig. 9(c) shows the T_{90} and τ_{res} under different intensities. A similar decay tendency is observed for T_{90} and τ_{res} when the intensity increased from 1.42 to 13.92 mW/cm^2 . High intensity causes a short response time.

4. Conclusion

R - T curves for an IGZO gas sensor were successfully observed with different LED intensities. At lower intensity, greater sensitivity and ΔR of the sensor were obtained. However, the τ_{res} and T_{90} are larger at lower intensity. According to the results, it possibly provides a good method for rapidly determining the target gas concentration by controlling light intensity; sensors can achieve

a fast response time using high light intensity. They can also show better sensitivity by using low light intensity. Similar results were also observed in other kinds of materials (TiO_2). Results show that the sensitivity of gas sensor of oxide semiconductor can be modulated by controlling the light intensity under LED continuous irradiation.

Acknowledgement

The authors thank the financial supports of the Ministry of Science and Technology of Taiwan (MOST 103-2112-M-005-002).

References

- [1] C.J. Weschler, Ozone in indoor environments: concentration and chemistry, *Indoor Air* 10 (2000) 269–288.
- [2] H.E. Endres, W. Göttler, R. Hartinger, S. Drost, W. Hellmich, G. Müller, Ch. Bosch-v. Braunmühl, A. Krenkow, C. Perego, G. Sberveglieri, A thin-film SnO_2 sensor system for simultaneous detection of CO and NO_2 with neural signal evaluation, *Sens. Actuators B* 36 (1996) 353–357.
- [3] F. Berger, J. Sanchez, O. Heintz, Detection of hydrogen fluoride using SnO_2 -based gas sensors: understanding of the reactional mechanism, *Sens. Actuators B* 143 (2009) 152–157.
- [4] Xiao Liu, Sitian Cheng, Hong Liu, Hu Sha, Daqiang Zhang, Huansheng Ning, A survey on gas sensing technology, *Sensors* 12 (2012) 9635–9665.
- [5] K. Arshak, E. Moore, G.M. Lyons, J. Harris, S. Clifford, A review of gas sensors employed in electronic nose applications, *Sens. Rev.* 24 (2004) 181–198.
- [6] N.E. Agbor, J.P. Cresswell, M.C. Petty, A.P. Monkman, An optical gas sensor based on polyaniline Langmuir–Blodgett films, *Sens. Actuators B* 41 (1997) 137–141.
- [7] Eduard Llobet, Gas sensors using carbon nanomaterials: a review, *Sens. Actuators B* 179 (2013) 32–45.
- [8] Basudam Adhikari, Sarmishtha Majumdar, Polymers in sensor applications, *Prog. Polym. Sci.* 29 (2004) 699–766.
- [9] M. Ogita, N. Saika, Y. Nakanishi, Y. Hatanaka, Ga_2O_3 thin films for high-temperature gas sensors, *Appl. Surf. Sci.* 142 (1999) 188–191.
- [10] J.F. Chang, H.H. Kuo, I.C. Leu, M.H. Hon, The effects of thickness and operation temperature on $\text{ZnO}:\text{Al}$ thin film CO gas sensor, *Sens. Actuators B* 84 (2002) 258–264.
- [11] Dae Jin Yang, George C. Whitfield, Nam Gyu Cho, Pyeong-Seok Choa, Il-Doo Kim, Howard M. Saltsburg, Harry L. Tuller, Amorphous InGaZnO_4 films: Gas sensor response and stability, *Sens. Actuators B* 171–172 (2012) 1166–1171.
- [12] Moon-Hwan Chang, Diganta Das, P.V. Varde, Michael Pecht, Light emitting diodes reliability review, *Microelectron. Reliab.* 52 (2012) 762–782.
- [13] Mirek Macka, Tomasz Piasecki, Purnendu K. Dasgupta, Light-emitting diodes for analytical chemistry, *Annu. Rev. Anal. Chem.* 7 (2014) 183–207.
- [14] Chi-Hwan Han, Dae-Woong Hong, Sang-Do Han, Jihye Gwak, Krishan C. Singh, Catalytic combustion type hydrogen gas sensor using TiO_2 and UV-LED, *Sens. Actuators B* 125 (2007) 224–228.
- [15] R.L. Shepherd, W.S. Yerazunis, K.T. Lau, D. Diamond, Novel surface mount LED ammonia sensors, *Proc. IEEE Sens.* 2 (2004) 951–954.
- [16] Chien-Chung Jeng, Paul J.H. Chong, Cheng-Chung Chiu, Guo-Jhen Jiang, Hung-Ju Lin, Ren-Jang Wu, Chiu-Hsien Wu, A dynamic equilibrium method for the SnO_2 -based ozone sensors using UV-LED continuous irradiation, *Sens. Actuators B* 195 (2014) 702–706.
- [17] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono, Room temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors, *Nature* 432 (2004) 488–492.
- [18] Hsiao-Wen Zan, Chang-Hung Li, Chun-Cheng Yeh, Ming-Zhi Dai, Hsin-Fei Meng, Chuang-Chuang Tsai, Room-temperature-operated sensitive hybrid gas sensor based on amorphous indium gallium zinc oxide thin-film transistors, *Appl. Phys. Lett.* 98 (2011) 253503.
- [19] Donghun Kang, Hyuck Lim, Changjung Kim, Ihun Song, Jaechoel Park, Amorphous gallium indium zinc oxide thin film transistors: sensitive to oxygen molecules, *Appl. Phys. Lett.* 90 (2007) 192101.
- [20] Wu Chiu-Hsien, Guo-Jhen Jiang, Kai-Wei Chang, Kue-Lin Chen, Effects of deposition temperature of amorphous In-Ga-Zn-O film on the sensitivity of ozone gas, *Sens. Actuators B* 211 (2015) 354–358.
- [21] K.C. Sanal, M. Majeesh, M.K. Jayaraj, Growth of IGZO thin films and fabrication of transparent thin film transistor by RF magnetron sputtering, *Proc. SPIE* 8818 (2013) 881814–881817.
- [22] Wu Ren-Jang, Zhe-Ming Li, Yong-Jun Qiu, Chien-Chung Jeng, Wu Chiu-Hsien, Sputtering layered $\text{TiO}_2/\text{SnO}_2$ films for ozone gas sensing property, *Sens. Lett.* 10 (2012) 726–730.
- [23] Wu Chiu-Hsien, Guo-Jhen Jiang, Cheng-Chung Chiu, Paul Chong, Chien-Chung Jeng, Wu Ren-Jang, Jan-Han Chen, Fast gas concentration sensing by analyzing the rate of resistance change, *Sens. Actuators B* 209 (2015) 906–910.