



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



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## 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 ( $\tau_{res}$ ) 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  $\text{TiO}_2$ . According to the results, the sensing properties of gas sensors can be modulated by controlling the light intensity.

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## 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  $\text{SnO}_2$  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

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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/cm<sup>2</sup> while maintaining constant  $O_3$  concentrations of 0.5 and 1 ppm. The lowest equilibrium resistance ( $R_a$ ), resistance change ( $\Delta R$ ), 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/cm<sup>2</sup>. 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.

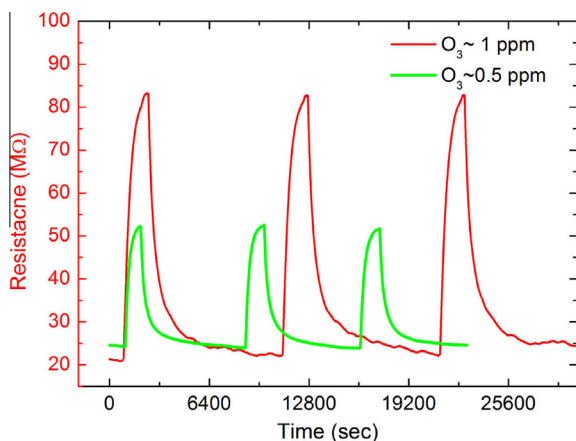
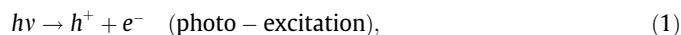
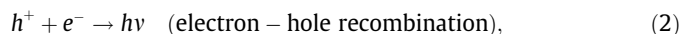
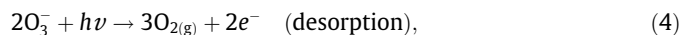


Fig. 1. The resistance–time curves of IGZO sensor at 0.5 and 1 ppm ozone.



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/cm<sup>2</sup>, 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/cm<sup>2</sup>; however, the change in  $R_g$  became small when the intensity was larger than 9.25 mW/cm<sup>2</sup>. 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  $dN_{\text{abs}}/dt$  and  $dN_{\text{des}}/dt$  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 ( $dN_{\text{des}}/dt$ ) 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;  $\Delta R$  and  $S$  are approximately 843 MΩ and 13.7, respectively, at 1.42 mW/cm<sup>2</sup> and approximately 93 MΩ and 8.29, respectively, at 13.92 mW/cm<sup>2</sup>. 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  $\Delta R$  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 ( $\tau_{\text{res}}$ ) 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

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