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Humidity Dependence of Commercial Thick and Thin-Film MOX Gas Sensors under UV Illumination †

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Abstract: Enhancing the performance of a chemo-resistive gas sensor is often challenging due to environmental humidity influencing its sensitivity and baseline resistance. One of the most promising ways of overcoming this challenge is through ultraviolet (UV) illumination of the sensing material. Most research has focused on using UV with in-house developed sensors, which has limited their widespread use. In this work, we have evaluated if UV can enhance the performance of commercially available MOX-based gas sensors. The performance of five different MOX sensors has been evaluated, specifically SGX Microtech MiCS6814 (thin-film triple sensor), FIGARO TGS2620 (*n*-type thick film), and Alphasense VOC sensor (*p*-type thick film). These sensors were tested towards isobutylene gas under UV light at different wavelengths (UV-278 nm and UV-365 nm) to investigate its effect on humidity, sensitivity, baseline drift, and recovery time of each sensor. We found the response time of thin-film sensors for reducing gases was improved by 70 s under UV- 365 nm at normal operating temperatures. In addition, all the sensors were left in a dirty environment and the humid-gas testing was repeated. However, due to their robust design, the sensitivity and baseline drift of all the sensors remained the same. This indicates that UV has only limited uses with commercial gas sensors.

Keywords: gas sensors; metal oxide semiconductors; thick films; thin films; UV irradiation

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1. Introduction

Metal oxide (MOX) gas sensors have been in continuous development since the first commercial metal oxide gas sensing device was first patented in 1972 by Taguchi [1]. Most of this work has been focused on improving the sensitivity and selectivity of such gas sensors by methods including doping, adding catalysts, and using different adhesives and binders. Part of this work has been to improve the humidity tolerance, operating conditions, and stability [2,3] of such sensors. Many MOX sensors are effected by environmental humidity, hindering their performance [4]. Illumination using ultraviolet (UV) light of the sensing material is one of the most promising ways of overcoming such challenges.

It is known that the working principle of a MOX gas sensor is based on a surface mechanism that can be explained by band theory. Predominantly, it is directly dependent on electron/hole pair exchange between the target gas and the sensing material. When the target gas is introduced, the oxygen atoms interact with the sensing material by either physical adsorption or in an atomic form (O^{2-} and O^{-}) depending on the operating temperature. However, only a minor part of the sensing surface interacts with the gas molecules under normal or dark conditions. Due to this, it causes only a small change in electrical conductance/resistance when exposed to a target gas. Illumination of ultraviolet rays enhances the surface chemical activity by increasing the number of charge carriers into the conduction band, providing a high number of active sites on the surface [3,4]. There has been a rapid development in UV sources that can be used for this purpose. One area that has seen significant improvement is in UV light emitting diodes (LEDs). They are particularly suited to gas sensor applications, due to their smaller size, with high

efficiency at a potentially low power. A LED is a *p*-*n* junction diode where the electrons and holes recombine at a junction to emit radiation at a wavelength depending on the *p* and *n* materials. The wavelength of a UV-LED varies from 210 nm (deep-UV) to 365 nm [5].

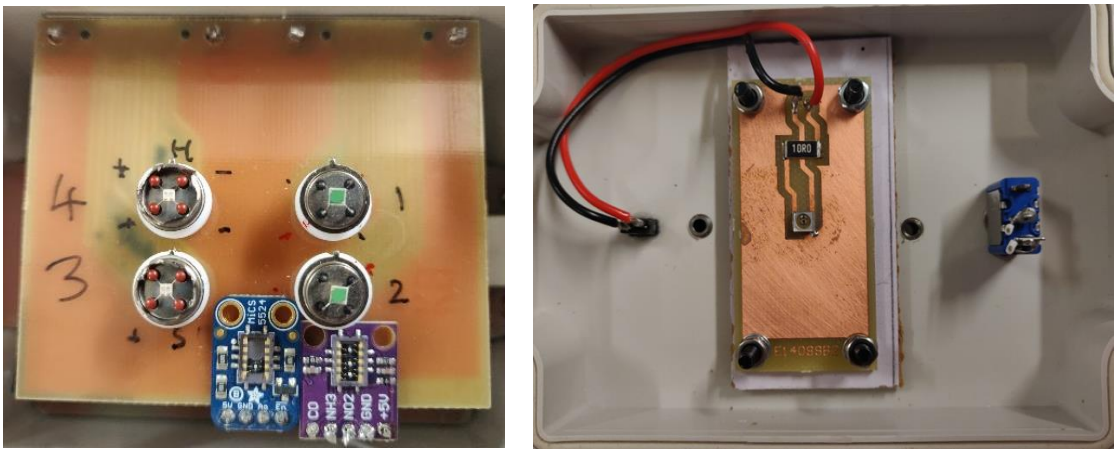
In the literature, most of the research on UV activated studies is based only on in-house fabricated sensors and not commercial devices. Thus, in this work, we evaluated a variety of different commercial gas sensors under UV light. The sensors used in this work were FIGARO TGS2620 (*n*-type thick film), Alphasense VOC MF1 sensor (*p*-type thick film) and SGX Microtech MiCS6814 (thin-film triple sensor). The SGX triple sensors contain three thin-film sensors for reducing gases (RED), NH_3 and oxidizing gases (OX). The specification of each of these sensors is given as per their respective datasheets [6–8].

To understand how different wavelengths of UV affects the sensitivity, we used two UV-LED sources illuminating at a 365 nm wavelength (NVSU233A-U365 Nichia, Tokushima, Japan) and a 278 nm wavelength (IN-C39CTKU1 Inolux, Santa Clara, US) onto the commercial sensors. The objective of this work was to evaluate if UV light enhances the performance and baselines of commercial MOX gas sensors under humid conditions. All the sensors were tested at relative humidity (RH) 10% and 85%, towards isobutylene gas. In addition, to understand if the UV light can cleanse the contaminated sensing surface, the sensors were made dirty in the environment using the miniature pumps for around two months and then the humid-gas testing was repeated under UV-365 nm.

2. Experimental Section

2.1. UV Box

An ad hoc UV box was developed for the study, as shown in Figure 1. This box contains a PCB board that can accommodate all the sensors inside it. This sensor development board contains an integrated resistor to create a potential divider with the sensors. The caps or the mesh present on the sensing material were removed so that the UV light falls directly onto the sensing material. There is a UV-LED source (UV-365 nm and UV-278 nm) attached to the lid. The box has two inlets and two outlets for the gas flow. The Alphasense VOC sensors were connected to AS-330 (Atmospheric Sensor Ltd., Essex, UK) sensor management system where the input parameters are managed through a PC based interface. FIGARO sensors and SGX triple sensors are powered at 5 V with an external power supply and their sensor voltages are measured by PicoLog 2000 series instrument and PicoLog 1012 series instrument, respectively, using a 2D 9-way connector. PicoLog is a multi-channel data acquisition instrument with up to 16 input data channels connected to a computer.



(**a**) (**b**)

Figure 1. (**a**) Sensor PCB board inside the UV box; (**b**) a UV-LED source.

2.2. Gas Testing

Gas testing was performed using a gas flow instrument containing 2 mass flow controllers (MFC) managed by a custom LABVIEW program. The carrier gas line is connected to zero-air and the target gas line is connected to a 50-ppm isobutylene gas cylinder. The desired gas concentration is achieved by setting the MFC flow rates. Humid air of 10% RH and 85% RH was generated by a water bubbler connected in line with the main gas lines, as illustrated in Figure 2. The water level in the bubbler maintains the final RH coming out through the gas lines.

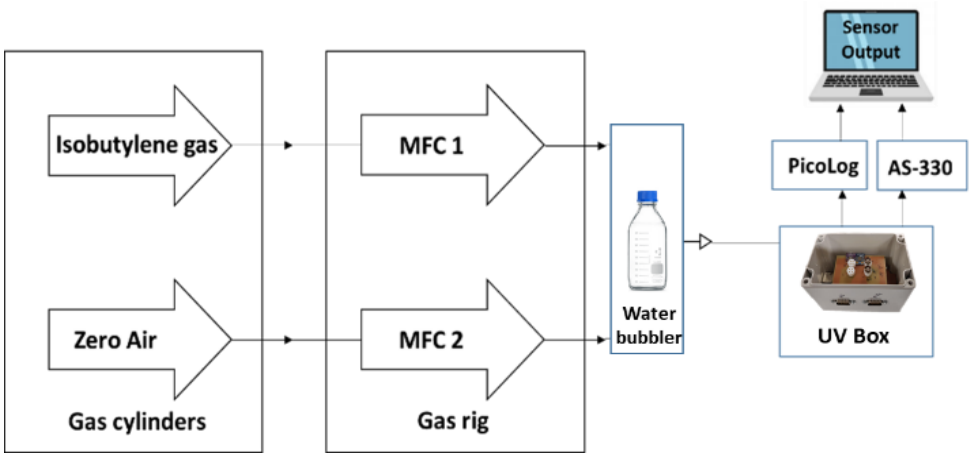
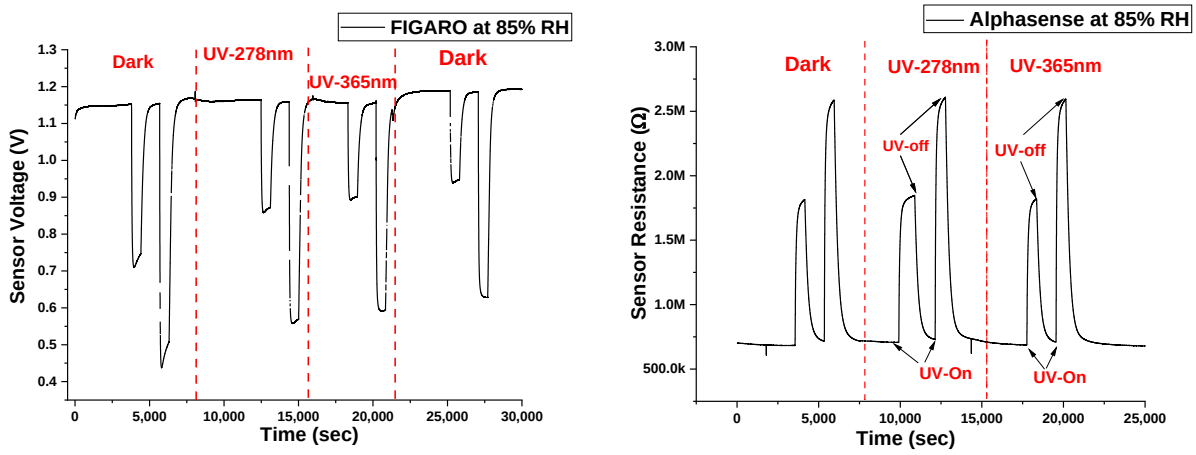


Figure 2. Experimental gas testing flow chart.

3. Results and Discussion

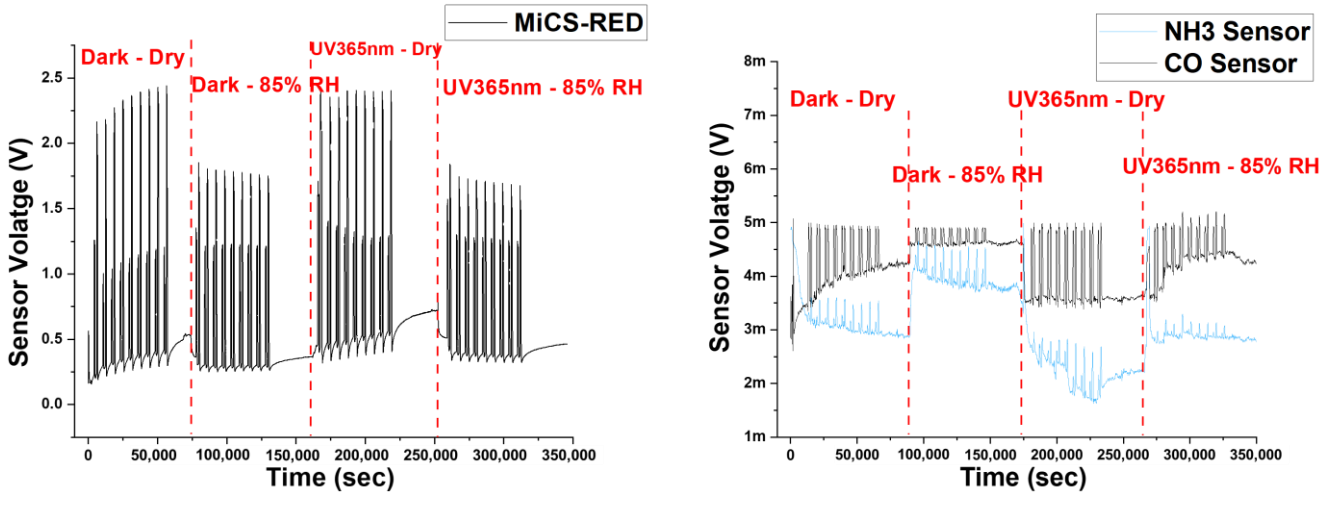
In the preliminary gas testing phase, all the sensors showed a baseline drift of 100–150% between dry and 85% RH conditions from its initial value. However, the sensor response and the response time did not vary. When compared between 85% RH and 10% RH condition the sensor baseline only increased by up to 5% for all the sensors. This behavior continued throughout the experiments. Initially, FIGARO TGS2620 and Alphasense VOC sensors were tested under dark, UV-278 nm and UV-365 nm conditions towards 10 and 50 ppm of isobutylene gas at 85% RH. FIGARO sensor was tested at continuous illumination of different UV lights and for the Alphasense VOC sensor, the UV was turned on only when the gas was introduced, as shown in Figure 3a,b, respectively. The sensor voltage decreased as the target gas was introduced for the FIGARO TGS2620 sensor as the sensing material is an *n*-type film while the sensor resistance of the Alphasense VOC sensor increased as it has a *p*-type film. The sensor response is calculated by n_g/n_a, where n_g = resistance or voltage (based on the sensor type) when target gas is introduced and n_a is resistance or voltage in air. The sensor response of FIGARO and Alphasense sensors remained unchanged at 1.26 (10 ppm) and 2.63 (10 ppm), respectively, under all the 3 conditions with a stable baseline. However, some results in terms of sensor response time were better under UV-365 nm than UV-278 nm. Therefore, we carried out the next set of experiments with UV-365 nm. Figure 4 shows the data for SGX MiCS 6814 triple sensors of three thin films at different conditions, dark and dry, dark and 85% RH, at UV-365 nm and dry and at UV-365 nm and 85% RH. The relative response (n_g/n_a) and response time (s) versus each condition for all the sensors are shown in Figure 5. The error bars indicate the standard deviation of each response after repeated testing at that condition. The response time and relative response did not improve under UV-365 nm for any of the sensors. However, at 85% RH, the MiCS Reducing sensor (MiCS-RED) and Alphasense VOC sensor reduced their response time by 70 s and 40 s under UV-365 nm, respectively. We propose that the quicker response time for the MiCS-RED sensor is associated with the film thickness. The MiCSRED is a thin film sensor, so the electric field lines travel along the top of the material and are interacting with the UV exposed sensing material.

The Alphasense device is thick film, so the electric field is unlikely to be passing through the top surface of the material. Even with its porous nature, only a small amount of UV light penetrated into the bulk of the material, resulting in a smaller effect. At that point in time, we did not have a reason for this reduction in response time. However, it is worth noting that this effect was not seen with a thick film SnO_2 sensing layer, but was observed with the MiCS-Red and Alphasense sensors (MiCS is *n*-type and Alphasense is *p*-type), which were alternative metal-oxides. Furthermore, this effect was only observed with sensors for reducing gases, and therefore, it is likely to be linked to the bandgap of the material involved. Further investigation is needed to discover why these materials have these properties. The relative response for MiCS-Red film was reduced from 4 to 3.3, while the relative response for Alphasense film remained constant throughout. However, no other sensor showed any sign of improvement under UV light in humid conditions. In addition, we allowed all the sensors to get dirty for more than 60 days. We used a miniature pump for this treatment and left the sensors on in their normal working condition, only to repeat the humid-gas testing under UV-365 nm. Here, all five devices also showed no change in performance post-treatment indicating that the UV light has only limited use for the commercial gas sensors.



(**a**) (**b**)

Figure 3. ISB Gas testing at 85% RH under different wavelengths of UV towards (**a**) FIGARO; (**b**) Alphasense VOC sensor.



(**a**) (**b**)

Figure 4. Humid gas testing at 4 different conditions (**a**) MiCS-RED; and (**b**) CO, NH3 thin film sensor.

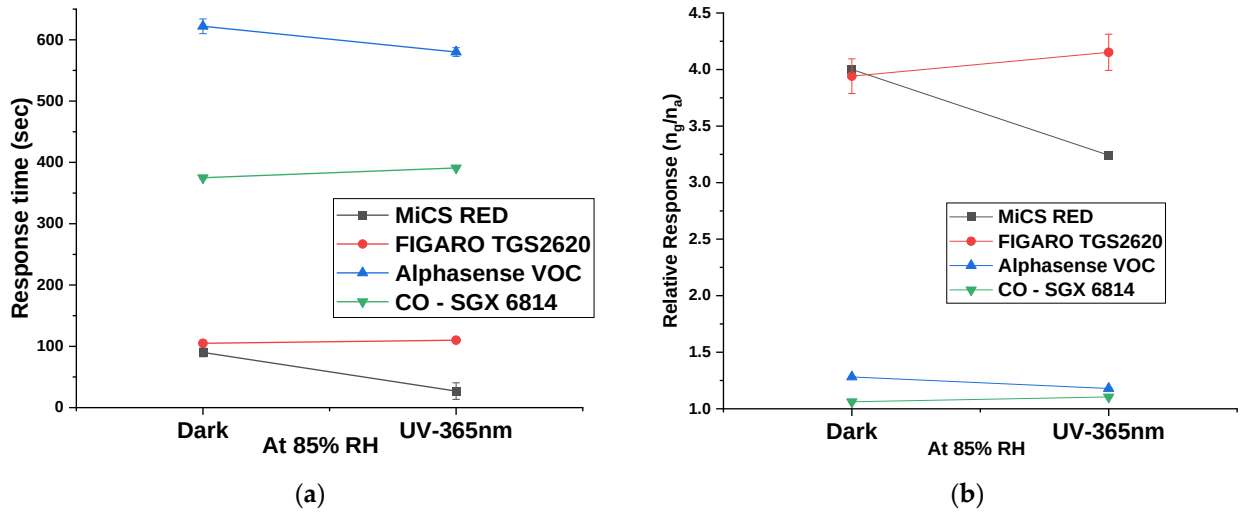


Figure 5. At 85% RH. (**a**) Response time versus dark and UV-365 nm; (**b**) relative response versus dark and UV-365 nm conditions.

Many factors influence sensor response and performance, however, there was no significant effect of UV light on these sensors. This could be attributed to their robust design and fabrication methods. Since these commercial sensors are developed to tackle real-life long-term gas testing, it is possible that the controlled lab environment with constant external conditions like temperature and humidity made it easy for the sensors to function stably. Furthermore, the irradiance power of the UV-LEDs could be an additional factor. We have used a UV-LED with a power of 2 mW (UV-278 nm) and 1030 mW (UV-365 nm). We suspect a higher power UV-LEDs could enhance the performance; however, more experiments need to be conducted to prove this.

The only sensor results that showed enhancement due to UV light, was in terms of response times for the MiCS-RED and Alphasense VOC sensors, as noted in Table 1. At 85% RH, the response time under dark conditions and UV-365 nm have improved from 87 s to 20 s and 622 s to 580 s for MiCS-RED film and Alphasense VOC sensor, respectively.

Table 1. Response time under dark and UV-365 nm at 85% RH for the respective commercial sensors.

Sensor	Response Time at Dark Condition	Response Time at UV-365 nm
MiCS-RED	90 s	20 s
Alphasense VOC Sensor	622 s	580 s

4. Conclusions

In this paper, we tested five commercial MOX based gas sensors under UV light at 278 nm and 365 nm wavelengths under two different humid conditions (10% RH and 85% RH) to study the effect of UV light on sensor performance. The sensors were tested towards 10 ppm and 50 ppm isobutylene gas. The results indicate the response time was enhanced for the MiCS-RED thin film and Alphasense VOC thick film sensors at 85% humid conditions under UV-365 nm. To further evaluate this, sensors were dirtied and repeated the humid-gas testing. However, the overall results suggest that due to the robust design and fabrication of these commercial sensors, UV light did not have any significant effect on baseline or sensitivity. It is our intention to do further study on the sensor morphology to understand this stable behavior. Thus, we conclude that UV light, under these conditions, does not add anything beyond simple resistance measurement.

Author Contributions: J.A.C. conceptualized the project. J.A.C. and S.K.A. designed the experiments. Gas testing and data analysis were carried out by S.K.A. Original draft preparation, review and editing of the manuscript were completed by S.K.A. and J.A.C. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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