IEEE Sensors Letters Volume 2(3) (2017)


# Ammonia gas optical sensor based on Lossy Mode Resonances

Dayron Armas[1]*, Pablo Zubiate[1], Carlos R. Zamarreño[1,2]** and Ignacio R. Matias[1,2]***

[1] *Electrical, Electronic and Communications Engineering Department, Public University of Navarra, Pamplona, NA 31006, Spain*
[2] *Institute of Smart Cities (ISC), Public University of Navarra, Pamplona, NA 31006, Spain*
** Student Member, IEEE*
*** Senior Member, IEEE*
**** Fellow, IEEE*

Received 1 Nov 2016, revised 25 Nov 2016, accepted 30 Nov 2016, published 5 Dec 2016, current version 15 Dec 2016. (Dates will be inserted by IEEE; “published” is the date the accepted preprint is posted on IEEE Xplore®; “current version” is the date the typeset version is posted on Xplore®).

**Abstract—**The fabrication and characterization of an ammonia ($NH_3$) gas optical sensor based on Lossy Mode Resonances (LMR) is presented in this work. A chromium (III) oxide ($Cr_2O_3$) thin film deposited onto a planar waveguide was used as LMR supporting coating. The obtained LMR shown a maximum attenuation wavelength or resonance wavelength centred in 673 nm. The optical properties of the coating can be modified as a function of the presence and concentration of $NH_3$ in the external medium. Consequently, the refractive index of the $Cr_2O_3$ thin film will change, producing a red-shift of the resonance wavelength. Obtained devices were tested for different concentrations of $NH_3$ as well as repetitive cycles. Concentrations as low as 10 ppbv of $NH_3$ were detected at room temperature. Machine learning regression models were used to mitigate the cross sensitivity of the device under temperature and humidity fluctuations.

**Index Terms—**Ammonia gas sensor, lossy mode resonance, planar waveguides, machine learning.

## I. INTRODUCTION

Ammonia ($NH_3$) is a substance that can be found in many household cleaning products, pesticides or fertilizers as well as in industrial and commercial refrigeration. Ammonia gas can be considered as a highly toxic and corrosive agent that can threat human health [1]. Moreover, ammonia is considered as an environmental pollutant since it is highly reactive and forms aerosols such as ammonium nitrate and ammonium sulphate when it reacts with nitric acid and sulphuric acid in the air, respectively [2]. Ammonia emissions can usually be attributed to fertilizers on agricultural crops and the decomposition of organic matter, among others. Some previous works have shown that vehicle traffic, urban wastewater treatment plants, municipal solid waste treatment plants, and some industries contribute to raise the level of ammonia gas in urban ambient air [3]. So, the detection of ammonia in urban areas is strategic for smart cities that demand precise, fast, robust, portable, reusable and cost-effective ammonia sensing devices. In this context, the European Union finances through the H2020 STARDUST project the study and development of this type of sensor systems that, together with other actions, helps make cities more sustainable [4], [5].

The optical device proposed in this work possesses all the previously mentioned requirements [6], such as high sensitivity, selectivity, immunity to electromagnetic interference, etc. Several techniques for measuring ammonia gas concentrations using optical sensors have been developed, such as those based on microstructured optical fiber [7], interferometry [8] and surface plasmon resonance [9] sensors.

Regarding resonance-based optical sensors, we can distinguish different types of resonances attending to the dielectric properties of the thin-film surrounding the optical waveguide [10]. One type of these resonances is known as Lossy Mode Resonance (LMR). LMRs occur when the real part of the thin film permittivity is positive and higher in magnitude than both its own imaginary part and that of the material surrounding the thin film. LMRs have been achieved using a wide variety of materials such as metal oxides like indium tin oxide (ITO) [11], titanium dioxide ($TiO_2$) [12], tin dioxide ($SnO_2$) [13] or polymers [14]. Moreover, as it is widely known, metal oxides have been used for the development and manufacturing of electronic and optical gas sensors, mostly based on $SnO_2$ and ITO [15], [16], [7].

In the next paragraphs, we show the utilization, for the first time in the literature, of chromium (III) oxide ($Cr_2O_3$) as the LMR supporting coating for the generation of LMR and, at the same time, the utilization of this thin-film as the transducing layer for ammonia gas sensing at room temperature.

## II. METHODS AND MATERIALS

### A. Coating fabrication

Chromium nitrate ($Cr(NO_3)_3$) and Polyvinyl alcohol (PVA) were purchased from Sigma-Aldrich Inc. The solvent used for the solutions was ultrapure deionized water (DIW) (18.1 M/cm).

It was prepared a solution of 2 g of PVA in 200 ml of DIW, and a solution of 8 g of chromium nitrate in 200 ml of DIW. Both solutes were stirred independently at room temperature for 1 hour. They were then mixed and stirred at room temperature for 3 hours. Then the

Corresponding author: D. Armas (dayron.armas@unavarra.es). Digital Object Identifier: 10.1109/LSEN.XXXX.XXXXXXX (inserted by IEEE).

solution was subjected to a final stir process at 50 °C for 5 more hours in order to obtain the sol-gel solution.

The LMR supporting-sensitive coating ($Cr_2O_3$) was fabricated onto coverslips (with dimensions 18 x 18 x 0.16 mm) using the dip-coating method. The coating fabrication process begins by dipping the coverslips in the solution for 1 hour and is followed by an annealing process in an oven at 200°C for 10 minutes to obtain a single layer. The process followed is detailed in [17] with the only difference that a conventional oven was used here. Previously described fabrication process is then repeated several times in order to increase the thickness of the coating. The final thickness of the coating will determine the location of the resonance wavelength. In particular, 8 cycles of dip-coating and annealing permitted to obtain an LMR with a resonance wavelength centred at 673 nm, which corresponded to the first Transverse Electrical (TE) polarization mode [18].

### *B. Ammonia sensor experimental setup*

The experimental setup used for the detection of ammonia gas is detailed in Fig. 1. The setup consisted of a typical transmission setup with an halogen light source (Takhi HP from Pyroistech S.A) connected to a multimode optical fiber (FT200EMT with 200/225 μm core/cladding diameter purchased from ThorLabs) that couples light to the edge of a $Cr_2O_3$ coated coverslip that acts both as planar waveguide and sensor. The light that goes through the sensor passes through a polarizer and is collected back by another multimode fiber that is connected to a CCD spectrometer (USB2000 from OceanOptics Inc.) operating in the visible-NIR wavelength range (400 and 1000 nm).

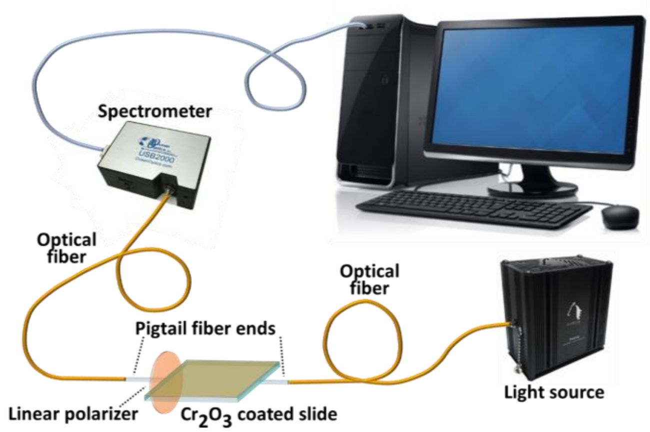


Fig. 1. Experimental measuring setup.

All the experiments were performed with the sensor placed in a 43 L sealed chamber. In order to guarantee the repeatability of the experiments, all actions were carried out in an ISO 5 clean room environment with the climatic conditions stabilized at 22+-0.5 °C of temperature and relative humidity of 50+-2 % during the measurements. Different tests were carried out in order to test the performance of the device when it was subjected to different concentrations of ammonia gas (30 % ammonia solution was purchased from Sigma-Aldrich Inc. and further diluted to a 1 % ammonia solution). A first test was used to determine the repeatability of the measurements. The test consisted of 3 cycles with the sensor subjected to 30 ppbv of ammonia with the corresponding recovery phases. A concentration of 30 ppbv of ammonia gas was achieved by pouring 128.55 ul of the ammonia solution into the closed chamber. Measuring process consisted of allowing the sensor to reach an equilibrium state after introducing the ammonia solution (response time), then opening the lid and allowing the sensor to reach an equilibrium state after recovering (recovery time). This was performed to detect the wavelength shifts of the LMR minimum dip during a time span. A second test was conducted to calibrate the sensor response to different ammonia gas concentrations in terms of wavelength shift of the LMR minimum dip. In this case, 4 cycles were recorded, corresponding to ammonia gas concentrations of 10, 30, 50 and 70 ppbv that were achieved by pouring 42.85, 128.55, 214.25 and 299.95 ul of the ammonia solution respectively.

Small fluctuations of the climatic conditions during the measurements (temperature and humidity) were mitigated using a regression model obtained from a dataset with a multiplicity of climatic conditions. The results obtained with the algorithm can help to predict the resonance wavelength shift associated to the climatic fluctuations and remove that contribution in order to determine the real ammonia gas concentration.

## III. RESULTS AND DISCUSSION

An LMR with a resonance wavelength located at 673 nm (TE polarization mode) was obtained after 8 dipping and annealing cycles of the substrates (see Fig. 2). The thin film thickness was measured with a Surftest SJ-410 surface roughness analyser from Mitutoyo. The measured thickness was 630 nm. It was in good agreement with the thickness of 8 cycles of the fabrication described in [17]. It is worth noting that, to our knowledge, no other work has been published where the generation of LMR is achieved using chromium oxide thin films. It is also important to remark that in contrast to other more sophisticated fabrication processes, such as sputtering, e-beam or atomic layer deposition, the thin film obtained here has been fabricated at room conditions with a simple annealing process at 200°C.

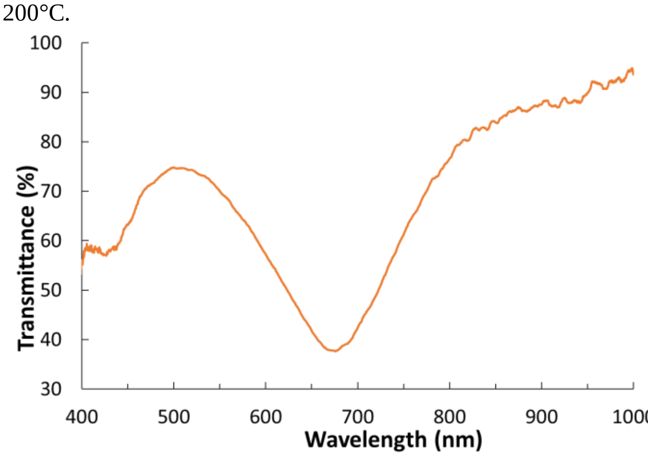


Fig. 2. Optical transmission spectrum measured with a thin film of $Cr_2O_3$ obtained after 8 repetitions of the deposition process. The LMR represented corresponds to the TE polarization mode.

Several examples can be found in literature on the use of Matlab regression models to compensate sensor measurement errors induced by different sources of error including temperature and humidity

[19]–[21]. The sensor response to variations in the climatic conditions (temperature and humidity) without $NH_3$ was recorded during a 7-hour span. Obtained dataset was used to compensate the small drifts of the temperature and relative humidity in the clean room, and the associated resonance wavelength shift during ammonia gas concentration measurements. Several types of machine learning regression models were trained with the obtained dataset using Matlab. The regression work was leveraged in Matlab own implementations contained in its Statistics and Machine Learning Toolbox version 12.2, specifically the *fitrauto* function.

The obtained models were then fed with the same training dataset to predict the LMR position. The model that best predicted the LMR position in comparison to the real measured position contained in the training dataset was a gaussian process regression model. The prediction error of that model is shown in Fig. 3, in terms of the difference between the LMR real position recorded in the training dataset, and the LMR position predicted by the model for the training dataset, along a time span. The maximum prediction error is of 0.15 nm. Here it is important to note that Matlab implementation of regression model training performs steps to avoid the overfitting phenomena. The selected model made the best prediction for the training dataset but there were several other trained models that made predictions totally deviated from the measured position.

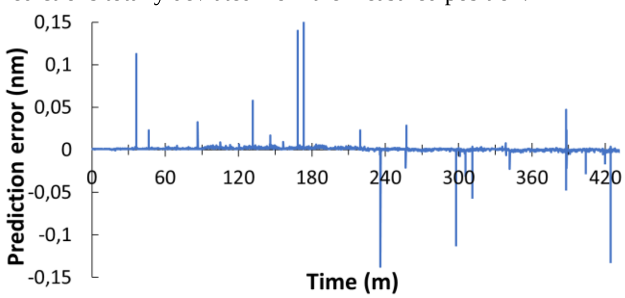


Fig. 3. Difference between the measured LMR position and the predicted position for the training dataset during a time span.

Consequently, this model was used to predict the resonance position during the experiments with different ammonia gas concentrations. Predicted resonance wavelength positions due to solely the temperature and relative humidity were then subtracted from the real resonance wavelength measured positions in order to obtain the resonance wavelength shifts associated to changes of ammonia gas concentration and not to humidity or temperature.

Regarding the sensing mechanism that takes place in the thin layer of $Cr_2O_3$ when it is subjected to ammonia gas, some authors agree that it is related to oxidization processes. Ammonia gas reacts with oxygen species adsorbed on the sensor surface, leading to a change in the material properties, utterly making a change in the effective refractive index of the waveguide and hence, shifting the resonance wavelength [22], [23], [24].

A first test to determine the repeatability of the measurements with the sensor is shown in Fig. 4. Resonance wavelength shifts towards larger wavelengths when it is subjected to ammonia gas, which is associated to an increase in the thin film refractive index associated to the oxidization processes. The average resonance wavelength shift for the 3 cycles is 6.17 nm. The differences between the first and the other cycles is associated to slight movements of the optical fibers that comprise the setup during the opening and closing of the chamber.

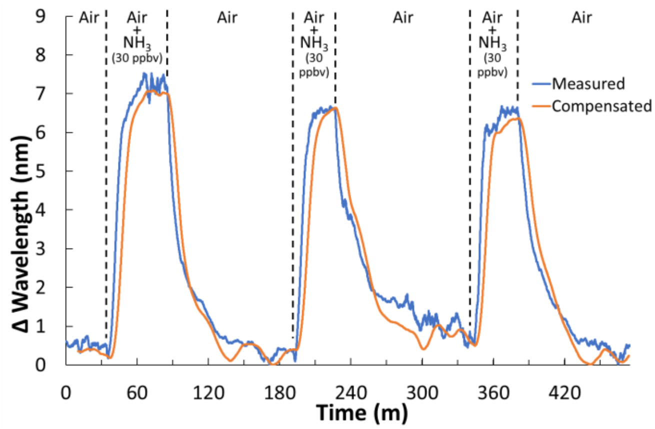


Fig. 4. LMR wavelength shift, measured and compensated, during 3 cycles of exposition to 30 ppbv of $NH_3$.

The response time (time between the 10 % and the 90 % of the sensor response) and recovery time (time from 90 % to 10 % of the sensor response during the recovery phase) were 15 and 33 minutes respectively. It is worth noting that the duration of the reaction phase includes the time it takes to the liquid $NH_3$ to evaporate and mix with the air contained in the chamber.

Although there are some differences between the 3 reaction and recovery cycles, they remained small in magnitude in comparison with the overall response of the sensor. For the second and third cycles there was a drop of 9.34 % and 12.04 % for the measured shift, and a drop of 7.04 % and 11.53 % for the compensated shift, respectively.

A second test to calibrate the sensor response is shown in Fig. 5. Here, the sensor was subjected to different $NH_3$ concentrations from 10 to 70 ppbv. The LMR experienced proportional shifts as a function of the ammonia gas concentration. The higher the $NH_3$ concentration, the longer the resonance wavelength shift. The response in one of the cycles, for 50 ppbv, differs from the expected response, possibly due to the slight movements of the optical fibers, as it was explained above.

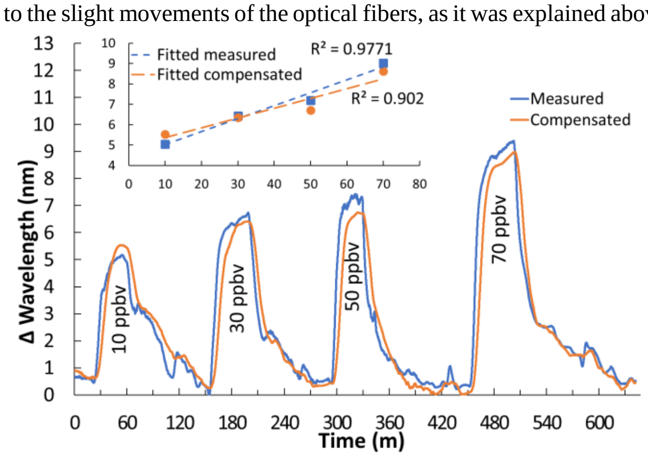


Fig. 5. LMR wavelength shift, measured and compensated, in the presence of 10, 30, 50 and 70 ppbv of $NH_3$. The inset plots the LMR wavelength shifts versus $NH_3$ concentrations (squares and circles), and the fitted curves (dashed lines), for the LMR shift values.

In the figure inset, the LMR wavelength shift data points are plotted versus the $NH_3$ concentration. Also, the fitted curves can be appreciated along with the values of $R^2$, for the measured and compensated LMR shifts. The respective values of $R^2$, 0.9771 and 0.902, reveal that the sensor as well as the compensation technique had almost linear behaviour, even under the influence of the evident deviation of the third measurement cycle response.

A dynamical range of 60 ppbv of $NH_3$ concentration was covered in Fig. 5 showing a resonance wavelength shift of 4.191 nm for the measured position and 3.388 nm for the compensated position. These results reveal a compensated sensitivity of the device to ammonia gas of 0.056 nm/ppbv (56 nm/ppmv).

Table 1 presents the ammonia sensors with the lowest level of detection (LOD) found in literature. The sensor proposed here has a LOD of 10 ppbv, comparable with the second, while working at room conditions of temperature and humidity, unlike the sensor with the best LOD which operated in a closed system.

Table 1. Ammonia sensors with the lowest LODs found in literature.

| Ref. | LOD | Sensor |
|---|---|---|
| [8] | 8.09 pptv | Interferometric PANI@$SnO_2$ nanocomposite |
| [25] | 10 ppbv | SPR/Grating in Ag/Yttria films |
| [26] | 25 ppbv | Capacitive Au/Ag-SnO2/SiO2/Si MIS |

## IV. CONCLUSIONS

Under the umbrella of the European H2020 Stardust project, this work shows some results related to detection of ammonia gas not only relevant in smart cities but in many other applications. In this work, ammonia gas sensors based on Lossy Mode Resonance (LMRs) have been fabricated by means of the deposition of a metal oxide, chromium oxide, onto coverslips.

It is worth noting that in the repeatability and calibration tests, the compensated LMR minimum dip position matches very closely the measured position due to the climatic control present in the laboratory where the experiments were carried out. Also, the regression model compensation technique could be easily applied to more dynamic environments like outdoor sensors for environmental monitoring.

This sensor has proven to be sensible to concentrations as low as 10 ppbv of ammonia, has good repeatability, a compensated sensitivity to ammonia gas of 56 nm/ppmv and the remarkable advantage of working at room temperature. These characteristics, together with its low cost, robustness and ease of mass production, make it a very suitable candidate to be used in real applications in smart city environments, among others.

## ACKNOWLEDGMENT

This work was supported by the Spanish Ministry of Science and Innovation through the FPI PRE2020-091797 grant, by the Spanish Agencia Estatal de Investigacion (AEI) with reference PID2022-137437OB-I00, and by the European Union’s Horizon 2020 Research and Innovation Programme (Stardust-Holistic and Integrated Urban Model for Smart Cities) under Grant Nº774094.

## REFERENCES

[1] Dutra F M, Rönnau M, Sponchiado D, Forneck S C, Freire C A, and Ballester E L C (2017), “Histological alterations in gills of Macrobrachium amazonicum juveniles exposed to ammonia and nitrite,” *Aquat. Toxicol.*, vol. 187, pp. 115–123.

[2] Kwak D, Lei Y, Maric R (2019), “Ammonia gas sensors: A comprehensive review,” *Talanta*, vol. 204, pp. 713–730.

[3] Reche C, Viana M, Karanasiou A, Cusack M, Alastuey A, Artiñano B, Revuelta M A, López-Mahía P, Blanco-Heras G, Rodríguez S, Sánchez de la Campa A M, Fernández-Camacho R, González-Castanedo Y, Mantilla E, Tang Y S, Querol X (2015), “Urban NH3 levels and sources in six major Spanish cities,” *Chemosphere*, vol. 119, pp. 769–777.

[4] “Stardust.” https://stardustproject.eu/ (accessed May 29, 2023).

[5] Astrain J J, Falcone F, Lopez A, Sanchis P, Villadangos J, Matias I R (2020), “Monitoring of Electric Buses within an Urban Smart City Environment,” *Proc. IEEE Sensors*, vol. 2020-October.

[6] Potyrailo R A, Hobbs S E, Hieftje G M (1998), “Optical waveguide sensors in analytical chemistry: Today’s instrumentation, applications and trends for future development,” *Fresenius’ Journal of Analytical Chemistry*, vol. 362, no. 4.

[7] López-Torres D, Lopez-Aldaba A, Elosúa Aguado C, Auguste J L, Jamier R, Roy P, López-Amo M, Arregui F J (2019), “Sensitivity optimization of a microstructured optical fiber ammonia gas sensor by means of tuning the thickness of a metal oxide nano-coating,” *IEEE Sens. J.*, vol. 19, no. 13, pp. 4982–4991.

[8] Shrivastav A M, Sharma G, Rathore A S, Jha R (2018), “Hypersensitive and Selective Interferometric Nose for Ultratrace Ammonia Detection with Fast Response Utilizing PANI@SnO2 Nanocomposite,” *ACS Photonics*, vol. 5, no. 11.

[9] Mishra S K, Tripathi S, Choudhary V, Gupta B D (2013), “Fiber optic ammonia gas sensor utilizing surface plasmon resonance of reduced graphene oxide,” in *Optics InfoBase Conference Papers*.

[10] Yang F, Sambles J R (1997), “Determination of the optical permittivity and thickness of absorbing films using long range modes,” *J. Mod. Opt.*, vol. 44, no. 6, pp. 1155–1164.

[11] Zamarreño C R, Del Villar I, Sanchez P, Hernaez M, Fernandez C, Matias I R, Arregui F J (2010), “Lossy-mode resonance-based refractometers by means of indium oxide coatings fabricated onto optical fibers,” *Fourth Eur. Work. Opt. Fibre Sensors*, vol. 7653, p. 76531W.

[12] Benítez M, Zubiate P, Del Villar I, Socorro-leránoz A B, Matías I R (2022), “Lossy Mode Resonance Based Microfluidic Platform Developed on Planar Waveguide for Biosensing Applications,” *Biosensors*, vol. 12, no. 6.

[13] Ozcariz A, Zamarreño C R, Zubiate P, Arregui F J (2017), “Is there a frontier in sensitivity with Lossy mode resonance ( LMR ) based refractometers ?,” *Sci. Rep.*, vol. 7, p. 10280.

[14] Zubiate P, Zamarreño C R, Del Villar I, Matias I R, Arregui F J (2016), “Tunable optical fiber pH sensors based on TE and TM Lossy Mode Resonances (LMRs),” *Sensors Actuators B Chem.*, vol. 231, pp. 484–490.

[15] Wang C, Yin L, Zhang L, Xiang D, Gao R (2010), “Metal Oxide Gas Sensors: Sensitivity and Influencing Factors,” *Sensors (Basel).*, vol. 10, no. 3, p. 2088.

[16] Gyger F, Hübner M, Feldmann C, Barsan N, Weimar U (2010), “Nanoscale SnO2 hollow spheres and their application as a gas-sensing material,” *Chem. Mater.*, vol. 22, no. 16, pp. 4821–4827.

[17] Al-Rashedi K, Farooqui M, Rabbani G (2018), “Characterizing crystalline chromium oxide thin film growth by sol-gel method on glass substrates,” *Orient. J. Chem.*, vol. 34, no. 4.

[18] Matias I R, Del Villar I, Corres J M (2023), “Lossy mode resonance based sensors in planar configuration: a review,” *IEEE Sens. J.*.

[19] Shuzan M N I, Chowdhury M H, Hossain M S, Chowdhury M E H, Reaz M B I, Uddin M M, Khandakar A, Mahbub Z B, Ali S H M (2021), “A Novel Non-Invasive Estimation of Respiration Rate from Motion Corrupted Photoplethysmograph Signal Using Machine Learning Model,” *IEEE Access*, vol. 9, pp. 96775–96790.

[20] Wei X, Ye H, Miao E, Pan Q (2022), “Thermal error modeling and compensation based on Gaussian process regression for CNC machine tools,” *Precis. Eng.*, vol. 77, pp. 65–76.

[21] De Vito S, Esposito E, Salvato M, Popoola O, Formisano F, Jones R, Di Francia G (2018), “Calibrating chemical multisensory devices for real world applications: An in-depth comparison of quantitative machine learning approaches,” *Sensors Actuators B Chem.*, vol. 255, pp. 1191–1210.

[22] Rout C S, Hegde M, Govindaraj A, Rao C N R (2007), “Ammonia sensors based on metal oxide nanostructures,” *Nanotechnology*, vol. 18, no. 20.

[23] Franke M E, Koplin T J, Simon U (2006), “Metal and metal oxide nanoparticles in chemiresistors: Does the nanoscale matter?,” *Small*, vol. 2, no. 1.

[24] Feng P, Wan Q, Wang T H (2005), “Contact-controlled sensing properties of flowerlike ZnO nanostructures,” *Appl. Phys. Lett.*, vol. 87, no. 21.

[25] Challener W A, Ollmann R R, Kam K K (1999), “A surface plasmon resonance gas sensor in a `compact disc’ format,” *Sensors Actuators B Chem.*, vol. 56, no. 3, pp. 254–258.

[26] Senapati M, Sahu P P (2020), “Meat quality assessment using Au patch electrode Ag-SnO2/SiO2/Si MIS capacitive gas sensor at room temperature,” *Food Chem.*, vol. 324, p. 126893.