Nb2O5 thin film-based conductometric sensor for acetone monitoring

Original
Nb2O5 thin film-based conductometric sensor for acetone monitoring / Lombardo, L., Donato, N., Grassini, S., Gullino, A., Moulaee, K., Neri, G., Parvis, M.. - ELETTRONICO. - 1:(2019), pp. 1-5. (2019 IEEE International Symposium on Medical Measurements and Applications, MeMeA 2019 Kadir Has University (KHU), tur 2019) [10.1109/MeMeA.2019.8802126].

Publisher:
Institute of Electrical and Electronics Engineers Inc.

Published
DOI:10.1109/MeMeA.2019.8802126

Title: Nb2O5 thin film-based conductometric sensor for acetone monitoring

Authors:

Luca Lombardo
Dept. of Electronics and Telecommunications, Politecnico di Torino, Torino, Italy

Nicola Donato
Department of Engineering, University of Messina, Messina, Italy

Sabrina Grassini
Dipartimento di Scienza Applicata e Technologia, Politecnico di Torino, Torino, Italy

Alessio Gullino
Dept. of Electronics and Telecommunications, Politecnico di Torino, Torino, Italy

Kaveh Moulaee
Department of Engineering, University of Messina, Messina, Italy

Giovanni Neri
Department of Engineering, University of Messina, Messina, Italy

Marco Parvis
Dept. of Electronics and Telecommunications, Politecnico di Torino, Torino, Italy

DOI: 10.1109/MeMeA.2019.8802126

Nb_2O_5 thin film-based conductometric sensor for acetone monitoring

Luca Lombardo
Dept. of Electronics and Telecommunications
Politecnico di Torino
Torino, ITALY
Email: luca.lombardo@polito.it

Nicola Donato
Department of Engineering
University of Messina
Messina, ITALY
Email: nicola.donato@unime.it

Sabrina Grassini
Dept. of Applied Science and Technology
Politecnico di Torino
Torino, ITALY
Email: sabrina.grassini@polito.it

Alessio Gullino
Dept. of Electronics and Telecommunications
Politecnico di Torino
Torino, ITALY
Email: alessio.gullino@polito.it

Kaveh Moulaee
Department of Engineering
University of Messina
Messina, ITALY
Email: k.movlaee@ut.ac.ir

Giovanni Neri
Department of Engineering
University of Messina
Messina, ITALY
Email: giovanni.neri@unime.it

Marco Parvis
Dept. of Electronics and Telecommunications
Politecnico di Torino
Torino, ITALY
Email: marco.parvis@polito.it

***Abstract*—Nowadays, effective detection of gases at ppm and ppb level is of crucial importance in a wide range of applications, such as industrial processes, environmental monitoring, public security and medical investigation. Several sensor types have been developed in last decades, among them the metal oxide gas sensors are the most promising for low-cost and portable applications, where good sensitivity and selectivity, together with small size are important constraints. The proposed conductometric gas sensor has been manufactured depositing a Nb_2O_5 thin film by plasma sputtering on a commercial alumina substrate with platinum interdigitated electrodes and heater which size is 3 mm × 6 mm with a thickness of 1 mm. The Nb_2O_5 thin film has been characterized by FE-SEM and XPS analysis. The sensor performance towards several target gases have been evaluated employing an experimental setup specifically developed for the characterization of gas sensors. The sensor exhibits good sensitivity towards acetone, a bio-marker found in human breath of diabetes patients. This makes the sensor promising in the non-invasive diagnosis of this kind of disease.**

***Index Terms*—gas sensing, acetone sensors, thin films**

I. INTRODUCTION

The detection of gases at ppm and ppb levels is nowadays of great importance in many fields ranging from industrial applications, to public security and medical investigations. Typical applications are the detection of toxic and dangerous gases, environmental monitoring and the diagnosis of several diseases by detecting gaseous bio-markers in the human breath. Great effort has been carried out in last years in order to develop effective and sensitive sensors for many different target gases. With this aim several different approaches were exploited for developing low-cost and highly performing sensors [1]–[3]; among them the most used are optical sensors, electrochemical sensors and metal oxide sensors.

In particular, metal oxide conductometric gas sensors have attracted the interest of researchers for decades because of their good performance, small size, flexibility, low-cost and easiness in their employment. The sensing principle of metal oxide gas sensors is based on the presence of vacancies on the sensing surface which behave as chemisorption centers for the oxygen normally present in the air and target gas molecules. According to the vacancy type, anionic or cationic, these oxides behave respectively as N-type or P-type semiconductors [4]–[7]. Molecules of a reducing or oxidizing gas, when in proximity of the sensing surface, reversibly and weakly bond to this vacancies with the consequent formation of surface states. This involves a change in the oxide conductance which is related to the number of absorbed gas molecules and thus to the gas concentration. The sensor response, or sensitivity, is usually defined in terms of relative change of sensor resistance: $S = R_a/R_g$ for reducing gases and $S = R_g/R_a$ for oxidizing gases, where R_a is the resistance of the sensor in presence of the only reference gas (typically air) and R_g the resistance in presence of the target gas [5]. A quite simple measurement system can be employed for measuring this relative change.

The chemisorption processes are strongly related to the chemical structure and morphology of the sensing layer. As consequence, these sensors can exhibit a selective behavior in respect to different target gases. Working temperature is also an important parameter which affects significantly sensitivity and selectivity of these sensors. In particular, temperature affects the chemisorption process resulting in a characteristic response-to-temperature bell-shaped relation. Initially, the sensor response increases with temperature due to the enhancement of sensing surface reactivity and the consequent increasing of the number of gas molecules bonded on the surface. However, also the desorption rate increases with the temperature so that it exists a specific temperature at which the desorption processes start to prevail on the adsorption ones and any further increasing of working temperature involves a reduction of the sensor response. This specific temperature, for a given sensing material, changes with the target gas. Typical values for working temperature go from $100\,^{\circ}\mathrm{C}$ to $600\,^{\circ}\mathrm{C}$, even though recently many works report of sensors working at room temperature [8], [9]. For this reason, measurement systems for conductometric gas sensors typically include a temperature control circuit, and the sensor itself has a dedicated heater. This characteristic of metal oxide gas sensors has been exploited for implementing several methods with allow one to discriminate between different gases by performing measurements at different temperatures [10]. Temperature also influences the response time of the sensor so that a suitable trade-off between temperature, power consumption, sensitivity and response time should be found for each specific application.

The sensitivity of such sensors depends on the number of vacancies available on the surface. Thus, for a given sensing material, increasing the surface to volume ratio can significantly increase the sensor response. This has been exploited in the last decade with the introduction of new technologies and methods for low cost deposition of thin films and the synthesis of nano-structures. Hundreds of novel sensors have been developed featuring very high sensitivity at a lower working temperature making these sensors suitable for new fields of application as the gas detection at the ppm and ppb levels, and portable applications, where low-power consumption is crucial [8], [11].

Several metal oxides have been recently studied and employed for the development of high-performance gas sensors. The most widespread are surely ZnO, SnO_2, TiO_2, CuO, V_2O_5, In_2O_3, and WO_3; often enriched with noble metals like gold, platinum and silver [12]–[15]. Instead, only few works deals with Nb_2O_5 and NbO even though its chemical and physical properties make it suitable for being employed as high-performing gas sensing material in metal oxide sensors [16], [17].

The proposed sensor is based on a Nb_2O_5 thin film deposited by plasma sputtering. Preliminary measurements revealed the good performance of the sensor especially toward acetone as target gas. Acetone is an highly volatile colorless and inflammable liquid compound mainly used as solvent in several fields. It is considered not toxic or harmful for human health in concentration down to $10000\ \mathrm{ppm}$. However, it can induce transitory health problems (such as irritation of eyes, skin and first respiratory system, and nausea) at higher concentrations [9]. Furthermore, the detection of acetone at ppm levels is employed as bio-marker in medical diagnosis of diabetes. Several studies showed that concentrations of acetone greater than $1\ \mathrm{ppm}$ in human breath are indicative of the disease [18], [19]. Thus, the development of effective, high-sensitive and low-cost acetone gas sensors to be employed in large scale non-invasive diagnosis of diabetes is a challenge of great importance.

II. EXPERIMENTAL DETAILS

The proposed sensor has been developed by depositing Nb-oxide thin films by reactive magnetron sputtering in a capacitively coupled parallel-plate-reactor with an asymmetric electrodes configuration onto a commercial alumina planar substrate. The reactor, shown in fig. 2, consists of a vacuum chamber made of stainless steel, a magnetron sputtering cathode connected to a RF (13.56 MHz) power supply through an impedance matching unit and a ground electrode, where the samples were positioned. The target material is stuck on the cathode, whose temperature is controlled by a cooling system, by means of a high conductive silver filled epoxy resin.

The depositions were performed by employing a Nb target (99.99% purity) fixed on the power electrode, with Ar (99.99% purity) and O_2 (99.99% purity) as discharge gases at the floating plasma temperature ($T < 60\,^{\circ}\mathrm{C}$) and $100\ \mathrm{mTorr}$ of total pressure. The depositions were performed with radio frequency powers in the range of 250 W to 500 W by varying the O_2/Ar flow rate ratio, as reported in table I. Before each deposition the target was pre-cleaned in an Ar discharge, closing the shutter in order to protect the IDE substrates from any contamination. Three different film samples (here denoted as $S1$, $S2$, and $S3$), have been prepared changing the deposition parameters and, indeed, individually characterized.

The alumina substrates are provided of two Platinum Interdigitated Electrodes (IDEs) on the top side, and of a Platinum heater on the back side. The overall dimensions of the substrate are $3\ \mathrm{mm} \times 6\ \mathrm{mm}$ with a thickness of $1\ \mathrm{mm}$. Fig. 1 shows the top and back sides of the IDEs substrate after the Nb_2O_5 thin film was deposited onto the top side. The film, being very thin, is almost totally transparent and is visible as darker area covering the IDEs.

Sensing tests were performed in a lab-scale apparatus which allows one to operate at controlled temperature performing resistance measurements, while the sensor is placed in a suitable test chamber under controlled atmosphere. Before the sensing tests, the sensors were conditioned in air for $2\ \mathrm{h}$ at $400\,^{\circ}\mathrm{C}$ in order to stabilize the sensing films. All measurements were performed under dry synthetic air (20% O_2 80% N_2), collecting the resistance of the sensing film by means of a Keithley 6487 picoammeter/voltage source.

III. MATERIAL CHARACTERIZATION

The niobium oxide film morphology and thickness were assessed by Field Emission Scanning Electron Microscopy (FESEM Supra 40 Zeiss). Images of the surface and cross-section of the niobium oxide layers (fig. 3) revealed a nanometric compact structure, composed by vertically oriented shaped rods with average diameter of about $15\ \mathrm{nm}$. The film thickness varies as a function of the RF power and deposition time in

TABLE I
DEPOSITION PARAMETERS FOR THE THREE Nb_2O_5 THIN-FILM SAMPLES.

Sample	Ar (sccm)	O_2 (sccm)	RF Power (W)	Dep. Time (min)	Thickness (nm)	Resistance (MΩ)
S1	50	20	500	30	500	100
S2	50	20	500	60	1100	60
S3	50	20	250	60	260	200

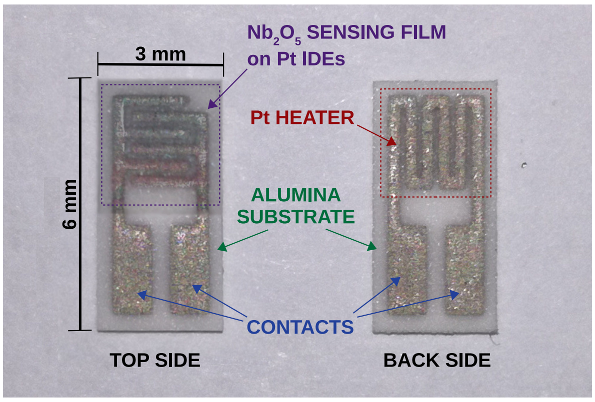

Fig. 1. Alumina substrate with platinum Interdigitated Electrodes (top side) and heater (back side) after the Nb_2O_5 thin film deposition. The deposited layer is visible as the darker area overlapping the top side.

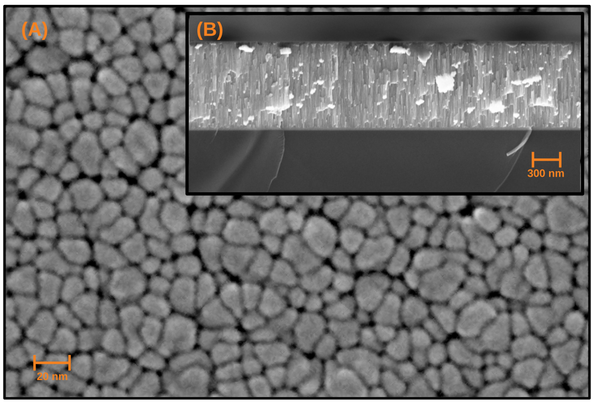

Fig. 3. FESEM image of the Nb_2O_5 thin film deposited on the sensor substrate (sample $S2$). (A) Surface morphology and (B) cross-section of the deposited film.

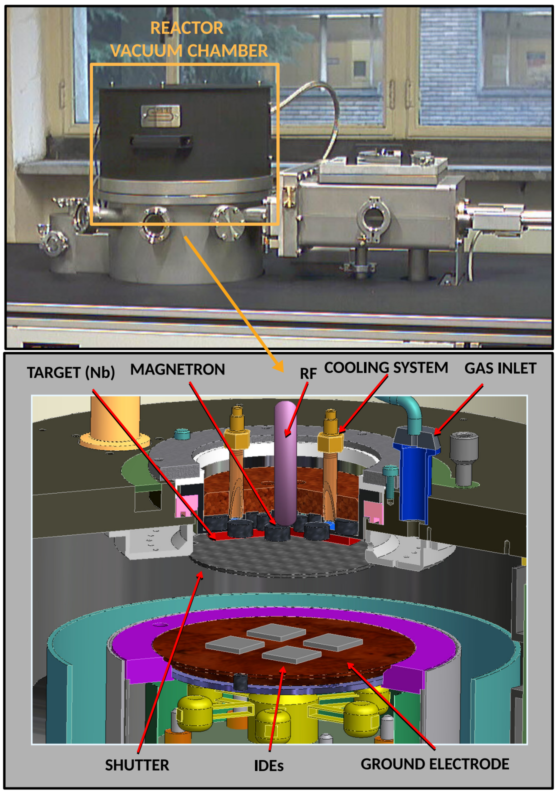

Fig. 2. Plasma reactor employed for the deposition of the Nb_2O_5 thin film and the block diagram on the inner part of the reaction chamber.

the range of $260\ \mathrm{nm}$ to $1100\ \mathrm{nm}$ (table I). This nanometric structure ensures a high and homogeneous distribution of chemisorption centers, which should lead to high sensitive material for gas detection.

Then the chemical composition of the Nb-oxide films and the Nb oxidation state were investigated by X-ray Photoelectron Spectroscopy (XPS). XPS measurements were carried out with a PHI Model 5000 electron spectrometer equipped with an aluminium anode ($1486\ \mathrm{eV}$) monochromatic source, with a power of $25\ \mathrm{W}$, and high-resolution scan with $11.75\ \mathrm{eV}$ pass energy. The instrument typically operates at pressures below $5 \times 10^{-8}\ \mathrm{mbar}$. The binding energies obtained by XPS analysis were corrected for sample charging by referencing the C 1s line to $284.6\ \mathrm{eV}$. High-resolution C 1s, O 1s and Nb 3d peaks were detected.

XPS spectra collected on the Nb-oxide thin films deposited in the different experimental conditions evidenced the same chemical composition of the sensing layer. Fig. 4 shows, as an example, the XPS survey spectrum of the Nb-oxide film deposited at $500\ \mathrm{W}$ (sample S2). It can be found two peaks at $207.1\ \mathrm{eV}$ and $209.8\ \mathrm{eV}$, respectively; the doublet at binding energy $207.1\ \mathrm{eV}$ (Nb $3d_{5/2}$) is characteristic of Nb^{5+} state and the peak at $209.8\ \mathrm{eV}$ (Nb $3d_{3/2}$) also confirms the film composition as diniobium(V) pentoxide, Nb_2O_5. Eventually, the Nb-oxide film were characterized by the electrical point of view by measuring the electrical resistance of the two contact of the IDEs, which resulted between $60\ \mathrm{M\Omega}$ and $200\ \mathrm{M\Omega}$ at room temperature.

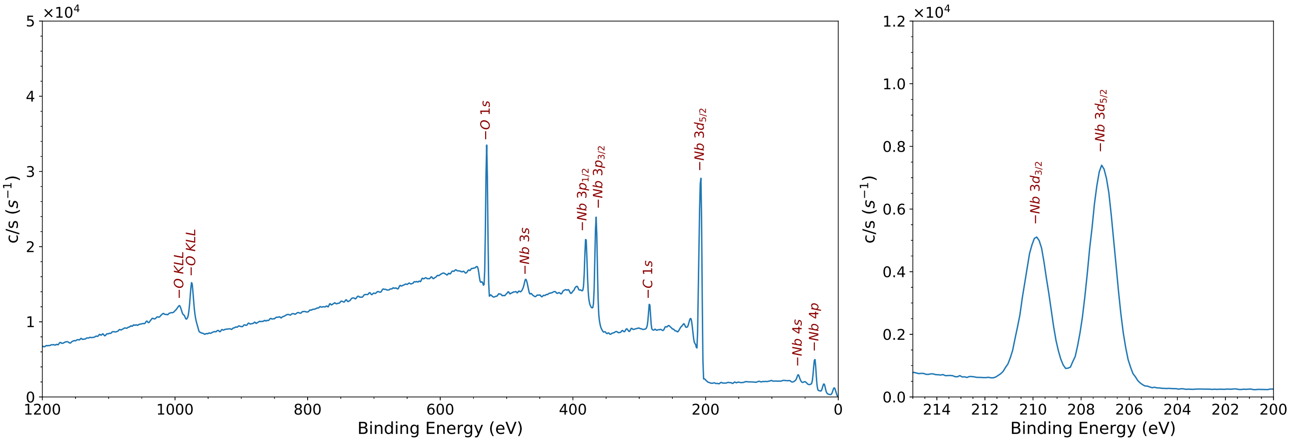

Fig. 4. XPS spectrum of the deposited Nb_2O_5 thin film (sample $S2$) and detail of the Nb_2O_5 characteristic peak.

IV. ACETONE SENSING TEST

Gas sensing tests of the Nb_2O_5 sensor toward low concentration of acetone in air were also performed. Fig. 5 illustrates the typical resistance variation of the sensor to $5\ \mathrm{ppm}$ of acetone at different temperatures. It can be noted the large decrease of the baseline resistance in presence of the reducing gas, which indicate the N-type behavior of the Nb_2O_5 sensing layer in this range of temperature. Furthermore, the response increases with decreasing temperature but, correspondingly, the rapid response and recovery observed at the higher temperature become longer at the lower one, even if the response/recovery time are short enough for practical application.

Transient curves of the Nb_2O_5 based gas sensor to different concentration of acetone in the range of $1\ \mathrm{ppm}$ to $40\ \mathrm{ppm}$ at $300\ {}^\circ\mathrm{C}$ are reported in fig. 6. Obviously, the response of the sensor to acetone increases with the raising of acetone concentration. The resistance variation is larger in the $1\ \mathrm{ppm}$ to $5\ \mathrm{ppm}$, which is particularly helpful for the determination of acetone in human breath. An increase in acetone vapor concentration leads to a saturation level due to the small thickness of the sensing layer, which determines the upper detection limit of the sensor.

Fig. 7 shows the relative response of the sensor at the different acetone concentrations. Here, it is clearly visible how the sensor response starts to saturate at acetone concentrations higher than $10\ \mathrm{ppm}$. A linear fitting (fig. 7, red line) can be satisfactory used to estimate the sensor response at acetone concentrations lower than $10\ \mathrm{ppm}$, instead, a second order fitting could be required at larger concentrations.

The reproducibility of the sensor signal is another important parameter. The good reproducibility of the developed sensor is demonstrated in fig. 8, which shows the sensor response to repeated pulses of acetone at a concentration of $5\ \mathrm{ppm}$.

V. CONCLUSIONS

Acetone can be used as bio-marker in the human breath for quick and non-invasive diagnosis of diabetes. Thus, the

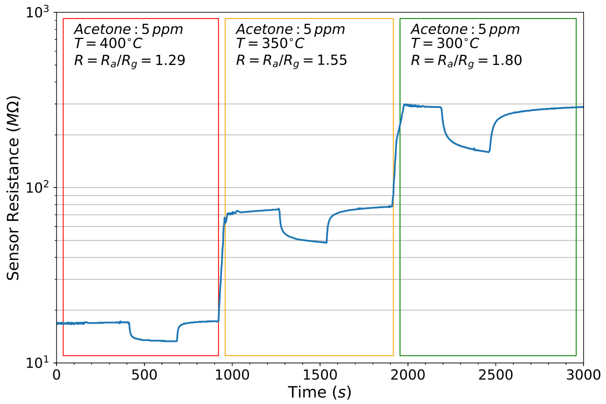

Fig. 5. Resistance variation and relative response of the sensor exposed to $5\ \mathrm{ppm}$ of acetone setting the working temperature at $300\ {}^\circ\mathrm{C}$, $350\ {}^\circ\mathrm{C}$ and $400\ {}^\circ\mathrm{C}$.

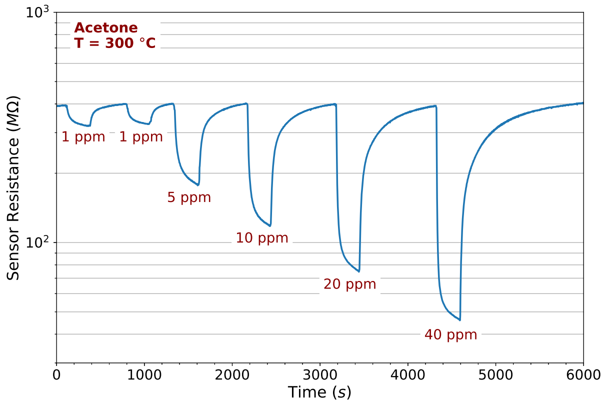

Fig. 6. Response of the Nb_2O_5 sensor operating at $300\ {}^\circ\mathrm{C}$ toward acetone in the range of $1\ \mathrm{ppm}$ to $40\ \mathrm{ppm}$.

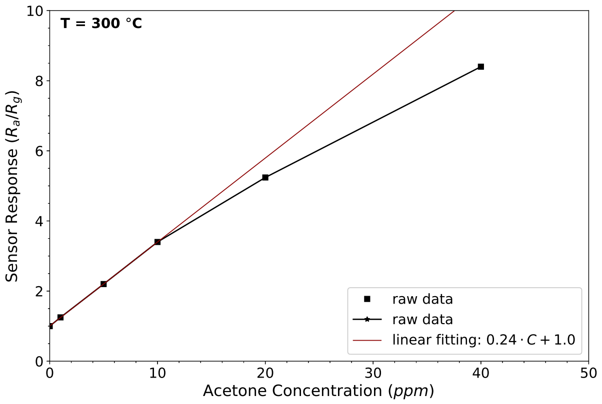

Fig. 7. Calibration curve and relative response of the sensor at acetone concentrations in the range of 1 ppm to 40 ppm. The response starts to saturate at a concentration greater than 10 ppm.

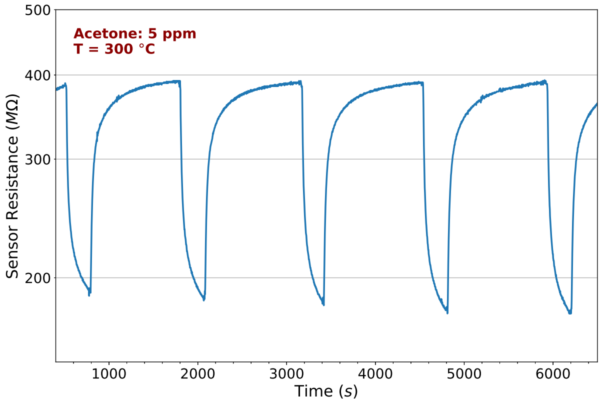

Fig. 8. Sensor response of the sensor to repeated pulses of acetone at a concentration of 5 ppm showing the good reproducibility of the sensor.

development of a gas sensor able to detect acetone at ppm level featuring small size, low cost, high-sensitivity and selectivity toward acetone is of great importance. The proposed conductometric gas sensor, manufactured by depositing a Nb_2O_5 thin film on a alumina substrate by plasma sputtering, shows good performance toward acetone. After the thin film has been characterized by FESEM and XPS analysis, the sensor has been tested in laboratory to assess its behavior in temperature and its response to acetone at concentrations in the range of 1 ppm to 40 ppm. The results demonstrate the good performance in terms of sensitivity, stability and reproducibility of the sensor.

REFERENCES

[1] S. Corbellini et al. ”Modified POF Sensor for Gaseous Hydrogen Fluoride Monitoring in the Presence of Ionizing Radiations”, IEEE Tr. on Instrumentation and Measurement, Vol 61, no 5, pp. 1201-1208, 2012

[2] S. Grassini et al. ”Gas monitoring in RPC by means of non-invasive plasma coated POF sensors”. JOURNAL OF INSTRUMENTATION, vol. 7, p. 1-11, 2012

[3] E. Angelini et al. ”Plasma modifed POF sensors for in situ environmental monitoring of museum environments.” APPLIED PHYSICS. A, MATERIALS SCIENCE & PROCESSING, vol. 100, p. 975-980, ,2010

[4] L. Chambon, A. Pauly, J.P. Germain, C. Maleysson, V. Demarne, A. Grisel, “A model for the responses of Nb_2O_5 sensors to CO and NH_3 gases”, Sensors and Actuators B, vol. 43, pp. 60–64, 1997.

[5] C. Wang, L. Yin, L. Zhang, D. Xiang, R. Gao, “Metal Oxide Gas Sensors: Sensitivity and Influencing Factors”, Sensors, pp. 2088–2016, 2010.

[6] N. Barsan, C. Simion, T. Heine, S. Pokhrel, U. Weimar, “Modelling of sensing ond transduction for P-type Semiconducting Metal Oxide Based Gas Sensors”, Journal of Electroceramics, vol. 25, issue 1, pp 11–19, August 2010.

[7] P.T. Moseley, “Solid State Gas Sensors”, Measurement Science and Technology, vol. 8, n. 3.

[8] J. Zhang, X. Liu, G. Neri, N. Pinna, “Nanostructured material for room-temperature gas sensors”, Advanced Materials, n. 28, pp. 795–831, 2016.

[9] K. Muthukrishnan, M. Vanaraja, S. Boomadevi, R.K. Karn, V. Singh, P.K. Singh, K. Pandiyan, “Studies on acetone sensing characteristics of ZnO thin film prepared by sol-gel dip coating”, Journal of Alloys and Compounds, n. 673, pp. 138–143, 2016.

[10] A. Vergara, E. Llobet, J. Brezmes, P. Ivanov, C. Can, I. Grcia, X. Vilanova, X. Correiga, “Quantitative gas mixture analysis using temperature-modulated micro-hotplate gas sensors: Selection and validation of the optimal modulating frequencies”, Sensors and Actuators B, n. 123, pp. 1002–1016, 2007.

[11] J. Lee, S. Mubeen, C.M. Hangartner, A. Mulchandani, W. Chen, N.V. Myung, “Selective and Rapid Room Temperature Detection of H 2 S Using Gold Nanoparticle Chain Arrays”, Electroanalysis, 23, n. 11, pp. 2623–2628, 2011.

[12] M.A. Andio, P.N. Browning, P.A. Morris, S.A. Akbar, “Comparison of gas sensor performance of SnO_2 nano-structures on micro hot-plate platforms”, Sensors and Actuators B, 165, pp. 13–18, 2021.

[13] Y. Li, X. Yu, Q. Yang, “Fabrication of TiO_2 nanotube thin films and their gas sensing properties”, Journal of Sensors, pp. 1–19, 2009.

[14] K.J. Choi, H.W. Jang, “One-dimensional oxide structures as gas-sensing materials: review and issues”, Sensors, n. 10, pp. 4083–4099, 2010.

[15] T. Hemalatha, S. Akilandeswari, T. Krishnakumar, S.G. Leonardi, G. Neri, N. Donato, “Comparison of Electrical and Sensing Properties of Pure, Sn- and Zn-Doped CuO gas sensors”, IEEE Transaction on Instrumentation and Measurement, 2018.

[16] Z. Wang, Y. Hu, W. Wang, X. Zhang, B. Wang, H. Tian, Y. Wang, J. Guan, H. Gu, “Fast and highly-sensitive hydrogen sensing of Nb_2O_5 nanowires at room temperature”, International Journal of Hydrogen Energy, n. 37, pp. 4526–4532, 2012.

[17] D. Rosenfeld, P.E. Schmid, S. Szles, F. Lvy, V. Demarne, A. Grisel, “Electrical transport properties of thin-film metal-oxide-metal Nb_2O_5 oxigen sensors”, Sensors and Actuators B, n. 37, pp. 83–89, 1996.

[18] C. Wang, A. Mbi, M. Shepherd, “A Study on Breath Acetone in Diabetic Patients Using a Cavity Ringdown Breath Analyzer: Exploring Correlations of Breath Acetone With Blood Glucoseand Glycohemoglobin A1C”, IEEE Sensors Journal, vol. 10, n. 1, January 2010.

[19] Z. Wang and C. Wang, “Is breath acetone a bio-marker of diabetes? A historical review on breath acetone measurements”, Journal of Breath Research, vol. 7, n. 3, 2013.