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TITANIUM DIOXIDE-BASED THICK FILM GAS SENSOR FOR HYDROGEN DETECTION

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of philosophy

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April 2020

Chair: Prof. Mohd Nizar bin Hamidon, PhD
Faculty: Institute of Advanced Technology

The need in detecting hazardous gases such as hydrogen has led to the development of simple, reliable and low cost of gas sensor for environmental monitoring and human safety. Excess amount of hydrogen in air can cause explosion, while longer exposure to the hydrogen can cause oxygen reduction in human body if the hydrogen replaces the oxygen in air. Therefore, the detection of hydrogen leakage has become essential issue in many industries. In detecting low concentration of hydrogen, a sensing material based on titanium dioxide (TiO_2) nanoparticles has been proposed in this study. A glass powder, B_2O_3 also was added into TiO_2 to obtain good adhesion of sensing film onto an alumina substrate. The TiO_2-B_2O_3 paste was prepared by mixing the sensing material with the organic binder. The organic binder used in this study was prepared using linseed oil, m-xylene and α-terpineol. The TiO_2-B_2O_3 gas sensor was developed using screen-printing technology to obtain porosity structures on the surface of the sensing film of a gas sensor, thus adsorption of the target gas will be increased and sensitivity of the gas sensor can be improved. Multi-walled carbon nanotube (MWCNT) and graphene nanoflakes with different ratios were added into TiO_2-B_2O_3 paste to enhance the conductivity of the gas sensor and to investigate the characteristics of the gas sensor, in term of sensitivity, response time, recovery time, optimum operating temperature and repeatability and stability properties of gas sensor to the hydrogen. The fabricated gas sensor was exposed to 100 – 1000 ppm of hydrogen and tested at different operating temperature (28°C, 50°C, 100°C, 150°C, 200°C and 250°C). Based on the TGA analysis, the optimum annealing temperature for the sensing film was achieved at 500°C with annealing time in 30 minutes under ambient air. The crystallinity of the sensing film after annealing treatment has been verified using EDX and XRD. Results showed the optimum operating temperature for the TiO_2-B_2O_3 gas sensor was occurred at 200°C. Additional of MWCNT into TiO_2-B_2O_3 has reduced the operating temperature from 150°C to 100°C, while addition of graphene nanoflakes has improved the sensitivity of TiO_2-B_2O_3 gas sensor to hydrogen. This study suggests that TiO_2-G1-B_2O_3 gas sensor as a better gas sensor for 100 – 700 ppm of hydrogen, while TiO_2-MWCNT5-B_2O_3 gas sensor as a better gas sensor for concentration above

of 1000 ppm of hydrogen. Overall, TiO_2-MWCNT5-B_2O_3 gas sensor is chosen as a promising material for gas sensor in detecting 100 – 1000 ppm of hydrogen at operating temperature of 100°C. The highest sensitivity values for TiO_2-MWCNT5-B_2O_3 gas sensor was achieved at operating temperature of 250℃ with sensitivity values are 6.97, 33.61, 67.64, 102.23 and 159.07 for 100 ppm, 300 ppm, 500 ppm, 700 ppm and 1000 ppm of hydrogen, respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

TITANIUM DIOKSIDA-BERDASARKAN PENDERIA GAS FILEM TEBAL BAGI PENGESANAN HIDROGEN

Oleh

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Keperluan dalam mengesan gas-gas berbahaya seperti hidrogen telah membawa kepada pembangunan penderia gas yang mudah, boleh dipercayai dan kos rendah bagi pemantauan alam sekitar dan keselamatan manusia. Lebihan kuantiti hidrogen di udara boleh menyebabkan letupan, sementara itu pendedahan yang lebih lama terhadap hidrogen dapat menyebabkan pengurangan oksigen dalam tubuh manusia jika hidrogen menggantikan oksigen di udara. Oleh itu, pengesanan kebocoran hidrogen telah menjadi isu penting dalam banyak industri. Dalam mengesanan kepekatan hidrogen yang rendah, bahan penderiaan berdasarkan nanopartikel titanium dioksida (TiO_2) telah dicadangkan di dalam kajian ini. Serbuk kaca, B_2O_3 juga telah dimasukkan ke dalam TiO_2 bagi mendapatkan lekatan filem penderiaan yang baik pada substrat alumina. Adunan TiO_2-B_2O_3 telah disediakan dengan mencampurkan bahan penderiaan dengan pengikat organik. Pengikat organik yang digunakan dalam kajian ini disediakan menggunakan minyak biji rami, *m-xylene* dan *α-terpineol*. Penderia gas TiO_2-B_2O_3 telah difabrikasi dengan menggunakan teknologi percetakan skrin bagi mendapatkan struktur keliangan pada permukaan filem pendria gas, maka penyerapan gas sasaran akan dapat ditingkatkan dan kepekaan penderia gas dapat dipertingkatkan. Nanotiub karbon multidinding (MWCNT) dan kepingan nano grafin dengan nisbah yang berbeza telah ditambah ke dalam adunan TiO_2-B_2O_3 bagi meningkatkan konduktiviti dan menyiasat ciri-ciri penderia gas khususnya kepekaan, masa tindak balas, masa pemulihan, suhu operasi optimum, sifat kebolehulangan dan kestabilan penderia gas terhadap hidrogen. Penderia gas telah didedahkan kepada 100 - 1000 ppm hidrogen dan diuji pada suhu operasi yang berbeza (28°C, 50°C, 100°C, 150°C, 200°C dan 250°C). Berdasarkan analisis TGA, suhu optimum bagi filem penderiaan telah dicapai pada 500°C dan masa penyepuh adalah 30 minit dibawah udara persekitaran. Pengkristalan yang tinggi bagi filem penderiaan selepas rawatan penyelepuhlindapan telah disahkan menggunakan EDX dan XRD. Keputusan menunjukkan suhu operasi optimum bagi penderia gas TiO_2-B_2O_3 berlaku pada 200°C. Penambahan MWCNT ke dalam TiO_2-B_2O_3 telah

dapat mengurangkan suhu operasi dari 150°C kepada 100°C, manakala penambahan kepingan nano grafin telah meningkatkan kepekaan penderia gas TiO_2-B_2O_3 terhadap hidrogen. Kajian ini menunjukkan bahawa penderia gas TiO_2-G1-B_2O_3 adalah penderia gas yang lebih baik bagi 100 - 700 ppm hidrogen, sementara penderia gas TiO_2-MWCNT5-B_2O_3 adalah penderia gas yang lebih baik bagi kepekatan gas di atas 1000 ppm hidrogen. Secara keseluruhan, penderia gas TiO_2-MWCNT5-B_2O_3 dipilih sebagai bahan yang menjanjikan bagi penderia gas dalam mengesan 100 - 1000 ppm hidrogen pada suhu operasi 100°C. Nilai kepekaaan tertinggi bagi penderia gas TiO_2-MWCNT5-B_2O_3 telah dicapai pada suhu operasi 250 ℃ dengan nilai kepekaan adalah 6.97, 33.61, 67.64, 102.23 dan 159.07 bagi 100 ppm, 300 ppm, 500 ppm, 700 ppm dan 1000 ppm hidrogen, masing-masing.

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I certify that a Thesis Examination Committee has met on (date of viva voce) to conduct the final examination of (student's name) on his (her) thesis entitled ("Title of Thesis") in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the (insert the name of relevant degree).

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

TiO_2	Titanium dioxide
B_2O_3	Boron oxide
Al_2O_3	Aluminium oxide
ZnO	Zinc oxide
SnO_2	Tin dioxide
Cr_2O_3	Chromium oxide
Ag	Silver
Pt	Platinum
Pd	Palladium
PbO	Lead oxide
H_2O	Water molecules
H_2	Hydrogen
Ni	Nickel
Au	Gold
MWCNT	Multi-walled carbon nanotube
FESEM	Field emission scanning electron microscope
EDX	Energy-dispersive x-ray
XRD	X-ray diffraction
BET	Brunauer-Emmett-Teller
sccm	Standard cubic centimeters per minute
ppm	Parts per million

CHAPTER 1

INTRODUCTION

1.1 Research Background

In recent years, hydrogen can be used as an alternative energy to replace fossil fuels for domestic and industrial and as a hydrogen fuel for transportation in rocket for space vehicle [1]. However, excessive amount of hydrogen in air, which exceed 4% can cause explosion because hydrogen is flammable [2]. As known, hydrogen is colorless, tasteless, and odorless, in which these characteristics make hydrogen cannot be detected by human senses. Even though hydrogen is a non-toxic gas, it also can cause oxygen reduction in human body if the hydrogen replaces the oxygen in air [3]. In other application, excessive amount of hydrogen in transformer oil, in the range of 700 – 1800 ppm indicates faults were occurred in a power transformer, whereas hydrogen concentration larger than 1800 ppm can cause transformer failure [4]. In year of 2008 until 2019, the number of SCI publications in detecting the hydrogen has increased to 930 publications. This increment showed that the hydrogen gas sensor has received large attention by researchers in every year due to the sustainability and safety purposes. Therefore, research in hydrogen gas sensor should be continued and a system that able to detect hydrogen leakage should be developed to avoid unpredictable explosion.

Various type of detection techniques in hydrogen gas sensor have been developed such as catalytic, thermal conductivity, electrochemical, resistance-based, work-function based, mechanical, optical and acoustic [5]. Among them, resistance-based types are the most common technique in detecting hydrogen gas sensor because of simple, low cost, robustness, simple measurement technique and offer good stability [6]. Other than that, optical and electrochemical technique also received great attention compared to the others technique. Optical method can produce high accuracy, however sophisticated instrument is needed and high cost is involved to increase their sizes [7]. Meanwhile, electrochemical gas sensor can be developed in low cost, despite cross-sensitivity and stability issue should be improved [8].

The most common material used in detecting of hydrogen is metal-oxide semiconductor such as tin dioxide (SnO2), zinc oxide (ZnO) and titanium dioxide (TiO2). It is because the ability of metal-oxide semiconductor to sense various type of gases, fast response and recovery time, low cost and easy fabrication process [9]. Reported that, metal-oxide also offers high sensitivity and good selectivity to the certain gases [10], [11]. Among metal-oxides gas sensor, TiO_2 has been reported in identifying low concentration of hydrogen as low as 1 ppm at room temperature [12]. Due to these advantages, TiO_2 has been selected as a promising sensing material to sense low concentrations of hydrogen in this study. Besides, TiO_2 also offers nontoxic, low cost, biocompatible and photo-corrosion resistant, which is practical material for hydrogen detection [12].

This thesis is concerned about the development of thick film gas sensor based on TiO_2 nanoparticles via screen-printing technique. The capability of the TiO_2 gas sensor in identifying various concentration of hydrogen at different operating temperatures was investigated. The performance of the gas sensor will be evaluated according to the important characteristics in designing a gas sensor such as sensitivity, optimum operating temperature, response time and recovery time, and repeatability and stability properties. The analysis will be calculated based on the data of the experimental results.

1.2 Problem Statement

Over the years, gas sensor based on TiO_2 has been used to detect various types of gases such as hydrogen, carbon monoxide, ammonia, nitrogen dioxide and volatile organic compounds. Different techniques have been applied to deposit a TiO_2 on a substrate of a gas sensor such as sputtering [12]–[15], dip-coating [16]–[20], screen-printing [20]–[22], doctor blade [23], and pulse laser deposition [24]. Among them, sputtering and dip-coating are the most common deposition technique applied for sensing film of gas sensor. Sputtering become the main selection of deposition technique because of high density, high adhesion, high hardness and good thickness uniformity on a substrate [25], while dip coating offers low-cost processing and ability to coat large complex shape [26]. However, sputtering process is very expensive and may facing problem with composition inhomogeneity and poor capability to provide good coverage for topographies with high aspect ratio [26], while for dip coating technique, size and thickness of sensing material during synthesis process become critical parameters to achieve maximum sensitivity of gas sensor [26]. Other than that, a few studies reported that screen-printing technique has been used to fabricate a thick film gas sensor based on TiO_2 to detect the hydrogen gas.

Initialization process also one of the important process that should be conducted in the early stage of gas sensor measurement in determining the important parameters in a gas sensor such as cycling time for carrier gas and target gas. Usually, the exposing time for the target gas is chosen longer, in which not regarding to the value of the response time of the gas sensor as reported in [12]. Other than that, shorter cycling time of the target gas also has been used, in which not observing until the saturated response was achieved [13]. Choosing suitable time to expose the target gas is important, in order to save time during the gas sensor measurement. Therefore, the suitable cycling time to flow of the target gas and carrier gas according to the value of response time and recovery time will be suggested in this study.

In a thick film gas sensor, usually a binder is needed to improve the mechanical strength of the film [27]. Common binder used in the thick film was based on the ethyl cellulose, however a few studies reported that a gas sensor based on the ethyl cellulose does not fully recover after exposed to the target gas [27]. Other than a binder, a small amount of glass powder also has been added into the paste of thick film gas sensor to improve the cohesion of particles and adhesion of the sensing film on a substrate [28]. The common glass powder used basically consists of PbO, where it requires higher firing temperature, in the range from 650℃ to 800℃, in other to be melted [29]–[31]. Higher firing temperature can remove the binder in the paste and melting the glass powder on a substrate, despite it also will make the size of nanostructures becomes larger, which it will affect the sensing mechanism of a gas sensor. Decrement of surface area will cause the capability of gas adsorption is getting difficulty on the surface of sensing film, thus the sensitivity of gas sensor will be reduced [32]. Therefore, an alternative of binder that able to produce good characteristic of gas sensor and a glass powder that has low melting point and also not affected the properties of TiO_2 should be suggested in this study. Boron oxide (B_2O_3) with melting point at 450℃ will be used as a glass powder in this study as an alternative to the conventional glass powder (PbO), in order to avoid high annealing temperature on the sensing film of a gas sensor, thus higher surface area can be achieved on the surface of the gas sensor.

Even though TiO_2 showed good response to hydrogen and able to work below operating temperature of 400℃, its low electrical n-type conductivity made it has higher resistivity, thus expensive equipment is needed to sense the target gas [33]. Various doping materials has been added to improve the conductivity and sensitivity of TiO_2 such as MWCNTs [18], [20] and chromium [34] to the target gas. Sonication [35], stirring [36], sonication and stirring [20], and sol-gel [34], [37] are the most common doping methods used to mix TiO_2 with additional material in a TiO_2 thick film gas sensor. However, limited studies were found based on paste-based and using the screen-printing technique. Thus, a simple method is needed to mixing the TiO_2 with doping material in the paste-based and applied for screen-printing technique without change of its properties and producing high sensitivity, faster response time and recovery time and reducing the operating temperature of TiO_2 gas sensor.

The work behind this research was initiated from the need to develop a low-cost, high sensitivity and able to operate at low operating temperature of TiO_2 gas sensor via screen-printing technology. Screen-printing technology has been chosen in this study because the ability of this deposition technique to produce porosity on the structure of the sensing film as compared with doctor blade and drop-casting in the thick film gas sensor. Porosity on the surface of the gas sensor is needed to increase adsorption of the target gas, thus enhance the sensitivity of the gas sensor. With this background and abstraction, a research work is needed to develop a high sensitivity gas sensor based on TiO_2, in which able to sense low concentration of hydrogen as low as 100 ppm and able to operate at low operating temperature as low as 100°C. This research work certainly can bring contribution to many application of hydrogen detection in many fields such as hydrogen fuel cell, dissolved gases in transformer oil and safety in vehicle.

1.3 Objectives of Study

This thesis focuses on the development of thick film gas sensor based on TiO_2 nanoparticles via screen-printing technique. The objectives in this study as follows:

i. To find the optimum annealing temperature of sensing film for gas sensor based on TiO_2-B_2O_3
ii. To develop a thick film gas sensor using screen-printing technique to monitor the various concentrations of hydrogen at different operating temperatures
iii. To investigate the characteristic of gas sensor in term of sensitivity, operating temperature, response and recovery time, and repeatability and stability properties by doping TiO_2-B_2O_3 with MWCNTs and graphene nanoflakes

1.4 Scope of work

In this study, fabrication of the gas sensor was developed using screen-printing technology with mesh thickness in the range of 8 – 12 µm and deposited on the 96% alumina substrate with thickness of 1 mm. The dimension of interdigitated electrode and sensing film were fixed to 4.0 mm x 4.0 mm and 4.5 mm x 4.5 mm, respectively, to compare the characteristic of gas sensor based on the different design of interdigitated electrode. The measurement of a gas sensor was conducted in a gas chamber. Concentrations of hydrogen was flowed in the range of 100 – 1000 ppm, while the synthetic air was flowed at 50 000 sccm. Minimum setting for mass flow controller is 5 sccm, where this value also equals to 100 ppm when mixed with the synthetic air, thus the lowest concentration of hydrogen used in this study is 100 ppm. The gas sensor also was tested at different operating temperatures which are 28°C, 50°C, 100°C, 150°C, 200°C and 250°C to investigate the characteristics of gas sensor to the hydrogen, in term of sensitivity, operating temperature, response and recovery time, and repeatability and stability properties. Maximum operating temperature for the temperature controller is 300°C, however the heating stage in the gas chamber is made by silicone, where it will start to deform at 280℃ and can cause temperature inconsistency on the heating stage. Therefore, the maximum operating temperature of the gas sensor used in this study is fixed to 250°C.

1.5 Thesis Outline

This thesis consists of six chapters. Chapter 1 describes the research background of the project, problem statement, objectives of study, scope of work and thesis outline. Chapter 2 provides a detailed review on the different types of detection method and deposition technique in a thick film gas sensor, relevant literatures relating to the current gas sensor used in detecting hydrogen and selection of TiO_2 as a sensing material for the gas sensor. Besides, mechanism of metal-oxide gas sensor to detect the hydrogen also will be discussed in this chapter.

Chapter 3 gives the details of the sensing materials and the fabrication of the gas sensor including the preparation of organic binder and TiO_2-B_2O_3 paste. Different design of interdigitated electrode and design of sensing film used for TiO_2-B_2O_3 gas sensor also will be proposed in this chapter. The experimental setup for measurement of gas sensor also has been explained in this chapter. Chapter 4 discusses the current-voltage characteristics for different designs of the interdigitated electrode on the sensing film for TiO_2-B_2O_3 gas sensor. The characterizations of organic binder, TiO_2-B_2O_3 paste and sensing materials also will be presented in this chapter.

Chapter 5 presents the characteristics of gas sensor to the various concentrations of hydrogen at different operating temperatures. The important characteristics in evaluating the performance of gas sensor such as sensitivity, optimum operating temperature, response time, recovery time and repeatability and stability properties were analyzed. The results of the best TiO_2-B_2O_3 gas sensor was compared with TiO_2-MWCNT-B_2O_3 gas sensor and TiO_2-G-B_2O_3 gas sensor. The best ratios of MWCNT and graphene nanoflakes added into TiO_2-B_2O_3 also will be suggested in this chapter. Finally, Chapter 6 concludes all the research findings and recommendation to the future project.

REFERENCES

[1] Esfandiar, A., Ghasemi, S., Irajizad, A., Akhavan, O., and Gholami, M. R. (2012). The decoration of TiO_2/reduced graphene oxide by Pd and Pt nanoparticles for hydrogen gas sensing. *Int. J. Hydrogen Energy*, 37(20):15423–15432.

[2] Gu, H., Wang, Z., and Hu, Y. (2012). Hydrogen Gas Sensors Based on Semiconductor Oxide Nanostructures. *Sensors*, 12, 5517–5550.

[3] Li, Z., Yao, Z., Haidry, A. A, Plecenik, T., Xie, L., Sun, L. and Fatima, Q. (2018). Resistive-type hydrogen gas sensor based on TiO_2 : A review. *Int. J. Hydrogen Energy*, 43(45): 21114–21132.

[4] Rogers, R. R. (1978). IEEE and IEC Codes to Interpret Incipient Faults in Transformers, Using Gas in Oil Analysis. *IEEE Trans. Electr. Insul.*, EI-13 (5): 349–354.

[5] Hubert, T., Boon-Brett, L., Black, G. and Banach, U. (2011). Hydrogen sensors - A review. *Sensors Actuators, B Chem.*, 157(2): 329–352.

[6] Tonezzer, M., Dang, L. T. T., Tran, H. Q. and Iannotta, S. (2018). Multiselective visual gas sensor using nickel oxide nanowires as chemiresistor. *Sensors Actuators, B Chem.*, 255: 2785–2793.

[7] Wang, X.-D. and Wolfbeis, O. S. (2013). Fiber-optic chemical sensors and biosensors (2008-2012). *Anal. Chem.*, 85(2): 487–508.

[8] Privett, B. J., Shin, J. H. and Schoenfisch, M. H. (2008). Electrochemical Sensors. *Anal. Chem*, 80(12): 4499–4517.

[9] Phanichphant, S. (2014). Semiconductor Metal Oxides as Hydrogen Gas Sensors. *Procedia Engineering*, 87: 795–802.

[10] Shao, C., Chang, Y. and Long, Y. (2014). High performance of nanostructured ZnO film gas sensor at room temperature. *Sensors Actuators, B Chem.*, 204: 666–672.

[11] Maziarz, W., Kusior, A. and Trenczek-Zajac, A. (2016). Nanostructured TiO_2-based gas sensors with enhanced sensitivity to reducing gases. *Beilstein J. Nanotechnol.*, 7(1): 1718–1726.

[12] Xia, X., Wu, W., Wang, Z. , Bao, Y., Huang, Z. and Gao, Y. (2016). A hydrogen sensor based on orientation aligned TiO_2 thin films with low concentration detecting limit and short response time. *Sensors Actuators, B Chem.*, 234: 192–200.

[13] Krško, O., Plecenik, T., Roch, T., Grančič, B., Satrapinskyy, L., Truchlý, M., Ďurina, P., Gregor, M., Kúš, P. and Plecenik, A. (2017).

Flexible highly sensitive hydrogen gas sensor based on a TiO_2 thin film on polyimide foil. *Sensors Actuators, B Chem.*, 240:1058–1065.

[14] Haidry, A. A., Schlosser, P., Durina, P., Mikula, M., Tomasek, M., Plecenik, T., Roch, T., Pidik, A., Stefecka, M., Noskovic, J., Zahoran, M., Kus, P. and Plecenik, A. (2011). Hydrogen gas sensors based on nanocrystalline TiO_2 thin films," *Cent. Eur. J. Phys.*, 9(5):1351–1356.

[15] Sharma, H., Singhal, R., Siva Kumar, V. V. and Asokan, K. (2016). Structural, optical and electronic properties of Ag–TiO_2 nanocomposite thin film. *Appl. Phys. A*, 122(1010): 1–9.

[16] Dutta, D., Hazra, S. K., Das, J., Sarkar, C. K. and Basu, S. (2015). Studies on p-TiO_2/n-graphene heterojunction for hydrogen detection. *Sensors Actuators, B Chem.*, 212: 84–92.

[17] Zhang, Y., Zeng, W., Ye, H., and Li, Y. (2018). Enhanced carbon monoxide sensing properties of TiO_2 with exposed (001) facet: A combined first-principle and experimental study. *Appl. Surf. Sci.*, 442: 507–516.

[18] De Luca, L., Donato, A., Santangelo, S., Faggio, G., Messina, G., Donato, N.and Neri, G. (2012). Hydrogen sensing characteristics of Pt/TiO_2/MWCNTs composites. *Int. J. Hydrogen Energy*, 37(2): 1842–1851.

[19] Peng, X., Wang, Z., Huang, P., Chen, X., Fu, X. and Dai, W. (2016). Comparative study of two different TiO_2 film sensors on response to H2 under UV light and room temperature. *Sensors*, 16(8):1–14.

[20] Sánchez, M. and Rincón, M. E. (2009). Sensor response of sol–gel multiwalled carbon nanotubes-TiO_2 composites deposited by screen-printing and dip-coating techniques. *Sensors Actuators B Chem.*, 140: 17–23.

[21] Zhang, M., Ning, T., Zhang, S., Li, Z., Yuan, Z. and Cao, Q. (2014). Response time and mechanism of Pd modified TiO_2 gas sensor. *Mater. Sci. Semicond. Process.*, vol. 17:149–154.

[22] Zhang, M., Yuan, Z., Song, J. and Zheng, C. (2010). Improvement and mechanism for the fast response of a Pt/TiO_2 gas sensor. *Sensors Actuators B Chem.*, 148: 87–92.

[23] Rane, S. S., Kajale, D. A., Arbuj, S. S., Rane, S. B. and Gosavi, S. W. (2017). Hydrogen, ethanol and ammonia gas sensing properties of nano-structured titanium dioxide thick films. *J. Mater. Sci. Mater. Electron.*, 28: 9011–9016.

[24] Stankova, N. E., Dimitrov, I. G., Stoyanchov, T. R. and Atanasov, P. A. (2007). Optical and gas sensing properties of thick TiO_2 films grown by laser deposition. *Appl. Surf. Sci.*, 254: 1268–1272.

[25] Wei, C.-H. and Chang, C.-M. (2011). Polycrystalline TiO_2 Thin Films with Different Thicknesses Deposited on Unheated Substrates Using RF Magnetron Sputtering. *Mater. Trans.*, 52(3): 554–559.

[26] Shukla, S., Patil, S., Kuiry, S. C., Rahman, Z., Du T., Ludwig, L., Parish, C. and Seal, S. (2003). Synthesis and characterization of sol-gel derived nanocrystalline tin oxide thin film as hydrogen sensor. *Sensors Actuators B Chem.*, 96(1–2): 343–353.

[27] Bakrania, S. D. and Wooldridge, M. S. (2009). The effects of two thick film deposition methods on tin dioxide gas sensor performance. *Sensors*, 9(9): 6853–6868.

[28] Guidi, V., Butturi, M. A., Carotta, M. C., Cavicchi, B., Ferroni, M., Malagù, C., Martinelli, G., Vincenzi, D., Sacerdoti, M. and Zen, M. (2002). Gas sensing through thick film technology. *Sensors Actuators B Chem.*, 84(1) :72–77.

[29] Patil, S. P., Patil, A. V., Dighavkar, C. G., Thakare, K. S., Borase, R. T., Nandre, S. J., Deshpande, N. G. and Ahire, R. R. (2015). Semiconductor metal oxide compounds based gas sensors : A literature review. *Front. Mater. Sci.*, 9(1): 14–37.

[30] Ehsani, M., Hamidon, M. N., Toudeshki, A., Abadi, M. H. S. and Rezaeian, S. (2016). CO_2 Gas Sensing Properties of Screen-Printed La_2O_3/SnO_2 Thick Film. *IEEE Sens. J.*, 16(18): 6839–6845.

[31] Abadi, M. H. S., Hamidon, M. N., Shaari, A. H., Abdullah, N., Wagiran, R. and Misron, N., Development of Nanocrystalline Laser Ablated Thick Film Array Gas Sensor. In *IEEE International Conference on Semiconductor Electronics*, 2010, pp. 88–91.

[32] Liu, X., Ma, T., Pinna, N. and Zhang, J. (2017). Two-Dimensional Nanostructured Materials for Gas Sensing. *Adv. Funct. Mater.*, 27(37): 1–30.

[33] Wisitsoraat, A., Comini, E., Sberveglieri, G., Wlodarski, W. and Tuantranont, A., TiO_2 Based Nanocrystalline Thin Film Gas Sensors Prepared by Ion-assisted Electron beam Evaporation. In *Proceedings of the 2nd IEEE International Conference on Nano/Micro Engineered and Molecular Systems*, 2007, pp. 109–112.

[34] Ruiz, A. M., Sakai, G., Cornet, A., Shimanoe K., Morante, J. R. and Yamazoe, N. (2003). Cr-doped TiO_2 gas sensor for exhaust NO_2 monitoring. *Sensors Actuators B Chem.*, 93(no. 1–3): 509–518.

[35] Ueda, T., Takahashi, K., Mitsugi, F. and Ikegami, T. (2009). Preparation of single-walled carbon nanotube/TiO_2 hybrid atmospheric gas sensor operated at ambient temperature. *Diam. Relat. Mater.*,18(2–3): 493–496.

[36] Frontera, P., Malara, A., Stelitano, S., Leonardi, S. G., Bonavita A., Fazio, E., Antonucci, P., Neri, G., Neri, F. and Santangelo, S. (2016). Characterisation and H_2O_2 sensing properties of TiO_2-CNTs/Pt electro-catalysts. *Mater. Chem. Phys.*, 170: 129–137.

[37] Santangelo, S., Faggio, G., Messina, G., Fazio, E., Neri, F. and Neri, G. (2013). On the hydrogen sensing mechanism of Pt/TiO_2/CNTs based devices. *Sensors Actuators B Chem.*, 178: 473–484.

[38] Heiland, G. (1957). On the influence of hydrogen on the electrical conductivity on the surface of zinc oxide crystals. *Zeitschrift für Phys.*, 148: 15–27.

[39] Mirzaei, A., Leonardi, S. G. and Neri, G. (2016). Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: A review. *Ceram. Int.*, 42(14): 15119–15141.

[40] Seiyama, T., Kato, A., Fujiishi, K. and Nagatani, M. (1962). A New Detector for Gaseous Components Using Semiconductive Thin Films. *Anal. Chem.*, 34(11): 1502–1503.

[41] Taguchi, N., Japan. Patent 45-38200, 1962.

[42] Korotcenkov, G. (2013). *Handbook of Gas Sensor Materials*, vol. 1. Springer.

[43] Tang, Y. M. and Ong, C. W. (2009). Room-temperature hydrogen-induced resistivity response of Pd/Mg–Ni films. *J. Mater. Res.*, 24(06): 1928–1935.

[44] Rashid, T. R., Phan, D. T. and Chung, G. S. (2013). A flexible hydrogen sensor based on Pd nanoparticles decorated ZnO nanorods grown on polyimide tape. *Sensors Actuators B Chem.*, 185: 777–784.

[45] Sun, P., Cao, Y., Liu, J., Sun, Y., Ma, J. and Lu, G. (2011). Dispersive SnO_2 nanosheets: Hydrothermal synthesis and gas-sensing properties. *Sensors Actuators B Chem.*, 156(2): 779–783.

[46] Xu, L., Chen, W., Jin, L. and Zeng, W. (2016). A novel SnO_2 nanostructures and their gas-sensing properties for CO. *J. Mater. Sci. Mater. Electron.*, 27(5): 4826–4832.

[47] Zhang, H., Zeng, W., Zhang, Y., Li, Y., Miao, B., Chen, W. and Peng, X. (2014). Synthesis and gas sensing properties of novel SnO_2 nanorods," *J. Mater. Sci. Mater. Electron.*, 25(11): 5006–5012.

[48] Huang, H., Tian, S., Xu, J., Xie, Z., Zeng, D., Chen, D. and Shen, G. (2012). Needle-like Zn-doped SnO_2 nanorods with enhanced photocatalytic and gas sensing properties. *Nanotechnology*, 23(10): 105502.

[49] Wang, G. X., Park, J. S., Park, M. S. and Gou, X. L. (2008). Synthesis and high gas sensitivity of tin oxide nanotubes. *Sensors Actuators B Chem.*, 131(1): 313–317.

[50] Zhang, J. and Gao, L. (2004). Synthesis and characterization of nanocrystalline tin oxide by sol-gel method. *J. Solid State Chem.*, 177(4–5): 1425–1430.

[51] Song, K. C. and Kang, Y. (2000). Preparation of high surface area tin oxide powders by a homogeneous precipitation method. *Mater. Lett.*, 42(5): 283–289.

[52] Acarbaş, Ö., Suvaci E., and Doğan, A. (2007). Preparation of nanosized tin oxide (SnO_2) powder by homogeneous precipitation. *Ceram. Int.*, 33(4): 537–542.

[53] Han, X., Zhang, B., Guan, S., Liu J., Zhang, X. and Chen, R. (2008). Gas-sensing properties of SnO_2 nanobelts synthesized by thermal evaporation of Sn foil. *J. Alloys Compd.*, 461(1–2): L26–L28.

[54] Tan, Y., Li, C., Wang, Y., Tang, J. and Ouyang, X. (2008). Fast-response and high sensitivity gas sensors based on SnO_2 hollow spheres. *Thin Solid Films*, 516(21): 7840–7843.

[55] Liewhiran, C., Tamaekong, N., Wisitsoraat, A. and Phanichphant, S. (2012). Highly selective environmental sensors based on flame-spray-made SnO_2 nanoparticles," *Sensors Actuators B Chem.*, 163(1): 51–60.

[56] Song, K. C. and Kim, J. H. (2000). Synthesis of high surface area tin oxide powders via water-in-oil microemulsions. *Powder Technol.*, 107(3): 268–272.

[57] Yazdi, M. A. P., Martin, N., Monsifrot, E., Briois, P. and Billard, A. (2015). ZnO nano-tree active layer as heavy hydrocarbon sensor: From material synthesis to electrical and gas sensing properties. *Thin Solid Films*, 596: 128–134.

[58] Korotcenkov, G. and Cho, B. K. (2013). Engineering approaches for the improvement of conductometric gas sensor parameters: Part 1. Improvement of sensor sensitivity and selectivity (short survey). *Sensors Actuators, B Chem.*, 188: 709–728.

[59] Gardon, M. and Guilemany, J. M. (2013). A review on fabrication, sensing mechanisms and performance of metal oxide gas sensors. *J. Mater. Sci. Mater. Electron.*, 24: 1410–1421.

[60] Kita, J., Engelbrecht, A., Schubert, F., Groß A., Rettig, F. and Moos, R. (2015). Some practical points to consider with respect to thermal conductivity and electrical resistivity of ceramic substrates for high-

temperature gas sensors. *Sensors Actuators B Chem.*, vol. 213: 541–546.

[61] Kita, J. and Moos, R. (2008). Development of LTCC-Materials and Their Applications - An Overview, 38(4): 219–224.

[62] Koch, E. and Dietzel, A. (2016). Skin attachable flexible sensor array for respiratory monitoring. *Sensors Actuators A Phys.*, 250: 138–144.

[63] Tournier, G. and Pijolat, C. (2005). Selective filter for SnO_2-based gas sensor: Application to hydrogen trace detection. *Sensors Actuators B Chem.*, 106(2): 553–562.

[64] Tomchenko, A. A., Harmer, G. P., Marquis, B. T. and Allen, J. W. (2003). Semiconducting metal oxide sensor array for the selective detection of combustion gases. *Sensors Actuators B Chem.*, 93(1–3): 126–134.

[65] Ippolito, S. J., Kandasamy, S., Kalantar-Zadeh, K. and Wlodarski, W. (2005). Hydrogen sensing characteristics of WO_3 thin film conductometric sensors activated by Pt and Au catalysts. *Sensors Actuators B Chem.*, 108(1–2): 154–158.

[66] Fleischer, M., Seth, M., Kohl, C.-D. and Meixner, H. (1996). A selective H_2 sensor implemented using Ga_2O_3 thin-films which are covered with a gas-filtering SiO_2 layer. *Sensors Actuators B Chem.*, 36(1–3): 297–302.

[67] Lee, A. P. and Reedy, B. J. (1999). Temperature modulation in semiconductor gas sensing. *Sensors Actuators B Chem.*, 60(1): 35–42.

[68] Patel, S. V., Mlsna, T. E., Fruhberger, B., Klaassen, E., Cemalovic, S. and Baselt, D. R. (2003). Chemicapacitive microsensors for volatile organic compound detection. *Sensors Actuators B Chem.*, 96(3): 541–553.

[69] Ishihara, T. and Matsubara, S. (1998). Capacitive type gas sensors. *J. Electroceramics*, 2(4): 215–228.

[70] Igreja, R. and Dias, C. J. (2006). Dielectric response of interdigital chemocapacitors: The role of the sensitive layer thickness. *Sensors Actuators B Chem.*, 115(1): 69–78.

[71] Denton, D. D., Senturia, S. D., Anolick, E. S. and Scheider, D. (1985). *Fundamental Issues in the Design of Polymeric Capacitive Moisture Sensors*. Philadelphia, PA, USA.

[72] Snow, E. S., Perkins, F. K., Houser, E. J., Badescu, S. C. and. Reinecke, T. L (2005). Chemical detection with a single-walled carbon nanotube capacitor. *Science*, 307(5717):1942-1945.

[73] Alberti, K. and Fetting, F. (1994). Zeolites as sensitive materials for dielectric gas sensors. *Sensors Actuators B Chem.*, 21(1): 39–50.

[74] Ishihara, T., Sato, S. and Takita, Y. (1995). Capacitive-type sensors for the selective detection of nitrogen oxides. *Sensors Actuators B Chem.*, 25(1–3): 392–395.

[75] Ishihara, T., Kometani, K., Mizuhara, Y. and Takita, Y. (1991). A new type of CO_2 gas sensor based on capacitance changes. *Sensors Actuators B Chem.*, 5(1–4): 97–102.

[76] Lee, S., Lee, G.-G., Kim, J. and. Kang, S.-J. L (2007). A novel process for fabrication of SnO_2-based thick film gas sensors. *Sensors Actuators B Chem.*, 123(1): 331–335.

[77] Y.-K. Jun, H.-S. Kim, J.-H. Lee, and S.-H. Hong, “CO sensing performance in micro-arc oxidized TiO2 films for air quality control,” *Sensors Actuators B Chem.*, vol. 120, no. 1, pp. 69–73, 2006.

[78] Suryawanshi, D. N., Patil, D. R. and Patil, L. A. (2008). Fe_2O_3-activated Cr_2O_3 thick films as temperature dependent gas sensors. *Sensors Actuators B Chem.*, 134(2): 579–584.

[79] Korotcenkov, G. (2014). *Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications. Volume 2, New Trends and Technologies*, Springer.

[80] White, N. (2017). Thick Films. *Handbook of Electronic and Photonic Materials*, Springer, pp. 707–721.

[81] Debataraja, A., Zulhendri, D. W., Yuliarto, B., Nugraha, Hiskia, and Sunendar, B. (2017). Investigation of Nanostructured SnO_2 Synthesized with Polyol Technique for CO Gas Sensor Applications. *Procedia Engineering*, 170: 60–64.

[82] Mohamad, I. S., Ismail, S. S., Norizan, M. N., Murad S. A. Z., and Abdullah M. M. A., (2017). ZnO Photoanode Effect on the Efficiency Performance of Organic Based Dye Sensitized Solar Cell. In *IOP Conference Series: Materials Science and Engineering*, 209: 1–7.

[83] Graf, M., Gurlo, A., Bârsan, N., Weimar, U. and Hierlemann, A. (2006). Microfabricated gas sensor systems with sensitive nanocrystalline metal-oxide films. *J. Nanoparticle Res.*, 8: 823–839.

[84] Sutka, A. and Gross, K. A. (2016). Spinel ferrite oxide semiconductor gas sensors. *Sensors Actuators B Chem.*, 222: 95–105.

[85] Bârsan, N., Hübner, M. and Weimar, U. (2011). Conduction mechanisms in SnO_2 based polycrystalline thick film gas sensors exposed to CO and H_2 in different oxygen backgrounds. *Sensors Actuators B Chem.*,157(2): 510–517.

[86] Bose, S., Chakraborty, S., Ghosh, B. K., Das, D., Sen, A. and. Maiti, H. S (2005). Methane sensitivity of Fe-doped SnO_2 thick films. *Sensors Actuators B Chem.*, 105(2): 346–350.

[87] Seo, M.-H., Yuasa, M., Kida, T., Huh, J.-S., Yamazoe, N. and Shimanoe, K. (2009). Detection of organic gases using TiO_2 nanotube-based gas sensors. *Procedia Chemistry*, 1: 192–195.

[88] [88] Turgut, E., Çoban, Ö., Sarıtaş, S., Tüzemen, S., Yıldırım, M. and Gür, E. (2018). Oxygen partial pressure effects on the RF sputtered p-type NiO hydrogen gas sensors. *Appl. Surf. Sci.*, 435: 880–885.

[89] Zhang, D., Sun, Y., Jiang C., and Zhang, Y. (2017). Room temperature hydrogen gas sensor based on palladium decorated tin oxide/molybdenum disulfide ternary hybrid via hydrothermal route. *Sensors Actuators B Chem.*, 242: 15–24.

[90] Zhou, Q., Chen, W. and Peng, S. (2013). Study on Sensing Properties of Pt/Fe/Zn Decorated SnO_2 Sensor for Dissolved CO in Transformer Oil. In *2013 Annual Report Conference on Electrical Insulation and Dielectric Phenomena*, pp. 1136–1139.

[91] Yang, X., Wang, W., Xiong, J., Chen, L. and Ma, Y. (2015). ZnO:Cd nanorods hydrogen sensor with low operating temperature. *Int. J. Hydrogen Energy*, 40(36): 12604–12609.

[92] Şennik, E., Ürdem, Ş., Erkovan, M. and Kilinç, N. (2016). Sputtered platinum thin films for resistive hydrogen sensor application," *Mater. Lett.*, 177: 104–107.

[93] Krško, O., Plecenik, T., Moško, M., Haidry, A. A., Ďurina, P., Truchlý, M., Grančič, B., Gregor, B., Roch, T., Satrapinskyy, L., Mošková, A., Mikula, M., Kúš, P. and Plecenik, A. (2015). Highly Sensitive Hydrogen Semiconductor Gas Sensor Operating at Room Temperature. *Procedia Engineering*, 120: 618–622.

[94] Öztürk, S. and Kılınç, N. (2016). Pd thin films on flexible substrate for hydrogen sensor. *J. Alloys Compd.*, 674: 179–184.

[95] Wu, C.-H., Zhu, Z., Chang, H.-M., Jiang, Z.-X., Hsieh, C.-Y. and Wu, R.-J. (2020). Pt@NiO core–shell nanostructure for a hydrogen gas sensor. *J. Alloys Compd.*, 814: 1–7.

[96] Nakate, U. T., Ahmad, R., Patil, P., Wang, Y., Bhat, K. S., Mahmoudi, T., Yu, Y. T., Suh, E.-K and Hahn, Y.-B (2019). Improved selectivity and low concentration hydrogen gas sensor application of Pd sensitized heterojunction n-ZnO/p-NiO nanostructures. *J. Alloys Compd.*, 797: 456–464.

[97] Kumar, R., Malik, S. and Mehta, B. R. (2015). Interface induced hydrogen sensing in Pd nanoparticle/graphene composite layers. *Sensors Actuators B Chem.*, 209: 919–926.

[98] Kabcum, S., Channei, D., Tuantranont, A., Wisitsoraat, A., Liewhiran, C. and Phanichphant, S. (2016). Ultra-responsive hydrogen gas sensors based on PdO nanoparticle-decorated WO_3 nanorods synthesized by precipitation and impregnation methods. *Sensors Actuators B Chem.*, 226: 76–89.

[99] Singh, G., Virpal, and Singh, R. C. (2019). Highly sensitive gas sensor based on Er-doped SnO_2 nanostructures and its temperature dependent selectivity towards hydrogen and ethanol. *Sensors Actuators B Chem.*, 282: 373–383.

[100] Hu, Y., Lei, J., Wang, Z., Yang, S., Luo, X., Zhang, G., Chen, W. and Gu, H. (2016). Rapid response hydrogen sensor based on nanoporous Pd thin films. *Int. J. Hydrogen Energy*, vol. 41(25): 10986–10990.

[101] Zhang, Z., Zou, X., Xu, L., Liao, L., Liu, W., Ho, J., Xiao, X., Jiang, C. and Li, J. (2015). Hydrogen gas sensor based on metal oxide nanoparticles decorated graphene transistor. *Nanoscale*, 7(22): 10078–10084.

[102] Chou, P.-C., Chen, H.-I., Liu, I.-P., Chen, W.-C., Chen, C.-C, Liou, J.-K., Lai, C.-J. and Liu, W.-C. (2015). On a Schottky diode-type hydrogen sensor with pyramid-like Pd nanostructures. *Int. J. Hydrogen Energy*, 40(29): 9006–9012.

[103] Behzadi pour, G. and Fekri aval, L. (2017). Highly sensitive work function hydrogen gas sensor based on PdNPs/SiO_2/Si structure at room temperature. *Results Phys.*, 7: 1993–1999.

[104] Dai, J., Peng, W., Wang, G., Xiang, F., Qin, Y., Wang, M., Yang, M., Deng, H. and Zhang, P. (2017). Improved performance of fiber optic hydrogen sensor based on WO3-Pd2Pt-Pt composite film and self-referenced demodulation method," *Sensors Actuators B Chem.*, vol. 249, pp. 210–216, 2017.

[105] Corso, A. J., Tessarolo, E., Guidolin, M., Gaspera, E. D., Martucci, A., Angiola, M., Donazzan, A. and Pelizzo, M. G. (2018). Room-temperature optical detection of hydrogen gas using palladium nano-islands," *Int. J. Hydrogen Energy*, vol. 43, no. 11, pp. 5783–5792, 2018.

[106] Banerjee, A. N. (2011). The design, fabrication, and photocatalytic utility of nanostructured semiconductors: Focus on TiO_2-based nanostructures. *Nanotechnol. Sci. Appl.*, vol. 4: 35–65.

[107] Diebold, U. (2003). The surface science of titanium dioxide. *Surf. Sci. Rep.*, 48(5–8): 53–229.

[108] Hanaor, D. A. H. and Sorrell, C. C. (2011). Review of the anatase to rutile phase transformation. *J. Mater. Sci.*, 46(4): 855–874.

[109] Mital, G. S. and Manoj, T. (2011). A review of TiO_2 nanoparticles. *Chinese Sci. Bull.*, 56(16):1639–1657.

[110] Tang, H., Prasad, K., Sanjines, R. and Levy, F. (1995). TiO_2 Anatase Thin-Films As Gas Sensors. *Sensors and Actuators B: Chemical*, 26(1–3): 71–75.

[111] Lu, C. and Chen, Z. (2009). High-temperature resistive hydrogen sensor based on thin nanoporous rutile TiO_2 film on anodic aluminum oxide. *Sensors Actuators B Chem.*, 140(1): 109–115.

[112] Kusior, A., Banas, J., Trenczek-Zajac, A., Zubrzycka, P., Micek-Ilnicka, A. and Radecka, M. (2018). Structural properties of TiO_2 nanomaterials. *J. Mol. Struct.*, 1157: 327–336.

[113] Galstyan, V., Comini, E., Faglia, G. and Sberveglieri, G. (2013). TiO_2 Nanotubes: Recent Advances in Synthesis and Gas Sensing Properties. *Sensors*, 13(11): 14813–14838.

[114] Lee, J., Hong Kim, D., Hong, S.-H. and Jho, J. Y. (2011). A hydrogen gas sensor employing vertically aligned TiO_2 nanotube arrays prepared by template-assisted method. *Sensors Actuators B Chem.*, 160(1): 1494–1498.

[115] Daniela D'Elia. PhD Thesis. Elaboration and study of TiO_2 nanostructures for hydrogen generation via photolysis of water. Paris Institute of Technology, 2011.

[116] Li, Z., Yao, Z., Haidry, A. A., Plecenik, T., Grancic, B., Roch, T., Gregor, M., and Plecenik, A. (2019). The effect of Nb doping on hydrogen gas sensing properties of capacitor-like Pt/Nb-TiO_2/Pt hydrogen gas sensors. *J. Alloys Compd.*, 806: 1052–1059.

[117] [117] Bahadur, N, Jain, K., Pasricha, R., Govind and Chand, S. (2011). Selective gas sensing response from different loading of Ag in sol-gel mesoporous titania powders. *Sensors Actuators B Chem.*, 159(1): 112–120.

[118] Wen, Z. and Tian-mo, L. (2010). Gas-sensing properties of SnO_2-TiO_2-based sensor for volatile organic compound gas and its sensing mechanism. *Phys. B Condens. Matter*, 405(5): 1345–1348.

[119] Carney, C. M.O., Yoo, S. and Akbar, S. A. (2005). TiO_2-SnO_2 nanostructures and their H2 sensing behavior," *Sensors Actuators B Chem.*, 108(1–2): 29–33.

[120] Mohammadi, M. R. and Fray, D. J. (2007). Semiconductor TiO_2-Ga_2O_3 thin film gas sensors derived from particulate sol-gel route. *Acta Mater.*, 55 (13): 4455–4466.

[121] Mak, T., Westerwaal, R. J., Slaman, M., Schreuders, H., Van Vugt, A. W., Victoria, M., Boelsma, C. and Dam, B. (2014). Optical fiber sensor for the continuous monitoring of hydrogen in oil. *Sensors Actuators, B Chem.*,190: 982–989.

[122] Dey, A. (2018). Semiconductor metal oxide gas sensors: A review," *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, 229: 206–217.

[123] Kaur, J., Roy, S. C. and Bhatnagar, M. C. (2007). Highly sensitive SnO_2 thin film NO_2 gas sensor operating at low temperature. *Sensors Actuators B Chem.*, 123(2): 1090–1095.

[124] Zhou, Q., Chen, W., Peng, S. and Su, X., Nano-tin oxide gas sensor detection characteristic for hydrocarbon gases dissolved in transformer oil. In *International Conference on High Voltage Engineering and Application*, 2012, pp. 384–387.

[125] Abdullah, Q. N., Yam, F. K., Hassan, Z. and Bououdina, M. (2014). Hydrogen gas sensing performance of GaN nanowires-based sensor at low operating temperature. *Sensors Actuators B Chem.*, 204: 497–506.

[126] Phan, D.-T. and Chung, G.-S. (2014). Effects of different morphologies of ZnO films on hydrogen sensing properties. *J. Electroceramics*, 32(4): 353–360.

[127] Pavlovsky, I. Hydrogen sensor for oil transformer health monitoring. In *IEEE Conference on Nanotechnology*, 2008, pp. 211–213.

[128] Chatterjee, A., Bhattacharjee, P., Roy, N. K and Kumbhakar, P. (2013). Usage of nanotechnology based gas sensor for health assessment and maintenance of transformers by DGA method. *Int. J. Electr. Power Energy Syst.*, 45(1): 137–141.

[129] Kim, J. C., Jun, H. K., Huh, J.-S. and Lee, D. D. (1997). Tin oxide-based methane gas sensor promoted by alumina-supported Pd catalyst. *Sensors Actuators B Chem.*, 45(3): 271–277.

[130] Shukla, S., Zhang, P., Cho, H. J., Seal, S. and Ludwig, L. (2007). Room temperature hydrogen response kinetics of nano-micro-integrated doped tin oxide sensor," *Sensors Actuators B Chem.*, 120(2): 573–583.

[131] Comini, E., Cristalli, A., Faglia, G. and Sberveglieri, G. (2000). Light enhanced gas sensing properties of indium oxide and tin dioxide sensors. *Sensors Actuators B Chem.*, 65(1–3): 260–263.

[132] Mishra, S., Ghanshyam, C., Ram, N., Bajpai, R. P. and Bedi, R. K. (2004). Detection mechanism of metal oxide gas sensor under UV radiation. *Sensors Actuators B Chem.*, 97(2–3): 387–390.

[133] Comini, E., Faglia, G. and Sberveglieri, G. (2001). UV light activation of tin oxide thin films for NO_2 sensing at low temperatures. *Sensors Actuators B Chem.*, 78(1–3): 73–77.

[134] Uddin, A. S. M. I., Yaqoob, U. and Chung, G. (2016). Dissolved hydrogen gas analysis in transformer oil using Pd catalyst decorated on ZnO nanorod array. *Sensors Actuators B Chem.*, 226: 90–95.

[135] Lu, G., Miura, N. and Yamazoe, N. (1996). High-temperature hydrogen sensor based on stabilized zirconia and a metal oxide electrode," *Sensors Actuators B Chem.*, 35(1–3): 130–135.

[136] Han, B., Liu, X., Xing, X., Chen, N., Xiao, X., Liu, S. and Wang, Y. (2016). A high response butanol gas sensor based on ZnO hollow spheres. *Sensors Actuators B Chem.*, 237: 423–430.

[137] Shukla, S., Ludwig, L., Parrish, C. and Seal, S. (2005). Inverse-catalyst-effect observed for nanocrystalline-doped tin oxide sensor at lower operating temperatures. *Sensors Actuators, B Chem.*, 104(2): 223–231.

[138] Al-Hardan, N., Abdullah, M. J., Abdul Aziz, A. and Ahmad, H. (2010). Low operating temperature of oxygen gas sensor based on undoped and Cr-doped ZnO films. *Appl. Surf. Sci.*, 256(11): 3468–3471.

[139] Kwon, H., Lee, Y., Hwang, S. and Kim, J. K. (2017). Highly-sensitive H_2 sensor operating at room temperature using Pt/TiO_2 nanoscale Schottky contacts. *Sensors Actuators B Chem.*, 241: 985–992.

[140] Penza, M., Martucci, C. and Cassano, G. (1998). NOx gas sensing characteristics of WO_3 thin films activated by noble metals (Pd, Pt, Au) layers. *Sensors Actuators B Chem.*, 50(1): 52–59.

[141] Espid, E. and Taghipour, F. (2017). Development of highly sensitive ZnO/In_2O_3 composite gas sensor activated by UV-LED. *Sensors Actuators B Chem.*, 241: 828–839.

[142] Jia, L. and Cai, W. (2010). Micro/nanostructured ordered porous films and their structurally induced control of the gas sensing performances. *Adv. Funct. Mater.*, 20(21): 3765–3773.

[143] Tong, X., Shen, W., Chen, X. and Corriou, J.-P. (2017). A fast response and recovery H2S gas sensor based on free-standing TiO_2 nanotube array films prepared by one-step anodization method. *Ceram. Int.*, 43(16): 14200–14209.

[144] Wang, L., Wang, Y., Yu, K., Wang, S., Zhang, Y. and Wei, C. (2016). A novel low temperature gas sensor based on Pt-decorated hierarchical 3D SnO_2 nanocomposites," *Sensors Actuators B Chem.*, 232: 91–101.

[145] Rani, S., Roy, S. C. and Bhatnagar, M. C. (2007). Effect of Fe doping on the gas sensing properties of nano-crystalline SnO_2 thin films. *Sensors Actuators B Chem.*, 122(1): 204–210.

[146] Shaalan, N. M., Rashad, M. and Abdel-Rahim, M. A. (2016). Repeatability of indium oxide gas sensors for detecting methane at low temperature. *Mater. Sci. Semicond. Process.*, 56: 260–264.

[147] Korotcenkov, G. (2007). Metal oxides for solid-state gas sensors: What determines our choice?. *Mater. Sci. Eng. B*, vol. 139(1): 1–23.

[148] Kim, H. W., Kwon, Y. J., Mirzaei, A., Kang, S. Y., Choi, M. S., Bang, J. H. and Kim, S. S. (2017). Synthesis of zinc oxide semiconductors-graphene nanocomposites by microwave irradiation for application to gas sensors. *Sensors Actuators B Chem.*, 249: 590–601.

[149] Williams, D. E. (1999). Semiconducting oxides as gas-sensitive resistors," *Sensors Actuators B Chem.*, 57: 1–16.

[150] Zakrzewska, K. and Radecka, M. (2017). TiO_2-Based Nanomaterials for Gas Sensing—Influence of Anatase and Rutile Contributions. *Nanoscale Res. Lett.*, 12(89): 1–8.

[151] Abadi, M. H. N. S. PhD Thesis. Development of nanocrystalline thick film gas sensors, Universiti Putra Malaysia, 2010.

[152] Ehsani, M. and Hamidon, M. N. (2014). Influence of Pt Doping on the Sensing Mechanism of La_2O_3/SnO_2 Thick Film for CO_2 Gas. *Int. J. Appl. Electron. Phys. Robot.*, 2(1): 6–7.

[153] Panta, R., Nanthamathee, C. and Ruangpornvisuti, V. (2018). Adsorption of hydrogen and hydrogen – containing gases on Pd– and Ag– single atoms doped on anatase TiO_2 (101) surfaces and their sensing performance. *Appl. Surf. Sci.*, 450: 112–121.

[154] Wongchoosuk, C., Wisitsoraat, A., Phokharatkul, D., Tuantranont, A. and Kerdcharoen, T. (2010). Multi-walled carbon nanotube-doped tungsten oxide thin films for hydrogen gas sensing. *Sensors*, 10(8): 7705–7715.

[155] Atchudan, R., Cha, B. G., Lone, N., Kim, J. and Joo, J. (2019). Synthesis of high-quality carbon nanotubes by using monodisperse spherical mesoporous silica encapsulating iron oxide nanoparticles. *Korean J. Chem. Eng*, 36(1): 157–165.

[156] Saidi, W., Hfaidh, N., Rasheed, M., Girtan, M., Megriche, A. and El Maaoui M., (2016). Effect of B_2O_3 addition on optical and structural properties of TiO_2 as a new blocking layer for multiple dye sensitive solar cell application (DSSC). *RSC Adv.*, 6(73): 68819–68826.

[157] Rong, Q., BY, Z., JC, H., ZQ, Z., Zhang, J. and QJ, L. (2018). Execellent Methanol Sensing Performance of Gas Sensor Based on Ag-$LaFeO_3$ Modified with Graphene. *J. Mol. Sci.*, 2(1:2): 1–5.

[158] Li, C., Lv, M., Zuo, J. and Huang, X. (2015). SnO_2 Highly Sensitive CO Gas Sensor Based on Quasi-Molecular-Imprinting Mechanism Design. *Sensors*,15(2): 3789–3800.

[159] Carrier, E. Photovoltaics: The Basics. In *A Comprehensive Guide to Solar Energy Systems*, 2018, Czech Technical University, pp. 151–179.

[160] Tauc, J., Grigorovici, R. and Vancu, A. (1966). Optical Properties and Electronic Structure of Amorphous Germanium. *Basic Solid State Phys.*, 15(2): 627–637.

[161] Valencia, S., Marín, J. M. and Restrepo, G. (2010). Study of the Bandgap of Synthesized Titanium Dioxide Nanoparticules Using the Sol-Gel Method and a Hydrothermal Treatment. *Open Mater. Sci. J.*, vol. 4: 9–14.

[162] Wang, G., Xu, L., Zhang, J., Yin, T. and Han, D. (2012). Enhanced photocatalytic activity of TiO_2 powders (P25) via calcination treatment. *Int. J. Photoenergy*, 2012(50) :1–9.

[163] Shi, Y.-J., Zhang, R.-J., Zheng, H., Li, D.-H., Wei, W., Chen, X., Sun, Y., Wei, Y.-F., Lu, H.-L., Dai, N. and Chen, L.-Y. (2017). Optical Constants and Band Gap Evolution with Phase Transition in Sub-20-nm-Thick TiO_2 Films Prepared by ALD. *Nanoscale Res. Lett.*, 12(243): 1–9.

[164] Mizukoshi, Y., Ohtsu, N., Semboshi, S. and Masahashi, N. (2009). Visible light responses of sulfur-doped rutile titanium dioxide photocatalysts fabricated by anodic oxidation. *Appl. Catal. B Environ.*, 91(1–2): 152–156.

[165] Grabowska, E., Zaleska, A., Sobczak, J. W., Gazda, M. and Hupka, J. (2009). Boron-doped TiO_2: Characteristics and photoactivity under visible light. *Procedia Chemistry*, 1(2): 1553–1559.

[166] Malliga, P., Pandiarajan, J., Prithivikumaran, N. and Neyvasagam, K. Effect of Film Thickness on Structural and Optical Properties of TiO_2 Thin Films. In *International Conference on Advanced Nanomaterials & Emerging Engineering Technologies*, 2013, pp. 488–491.

[167] Domtau, D. L., Simiyu, J., Ayieta, E. O., Muthoka, B. and Mwabora, J. M. (2016). Optical and Electrical Properties Dependence on Thickness of Screen-Printed TiO_2 Thin Films. *J. Mater. Phys. Chem.*, 4(1): 1–3.

[168] Scarsella, M., Bracciale, M. P., De Caprariis, B., De Filippis, P., Petrullo, A., Pronti, L. and Santarelli, M. L. (2017). Improved photocatalytic properties of doped titanium-based nanometric oxides. *Chem. Eng. Trans.*, 60: 133–138.

[169] Sheini, N. A, and Rohani, M. (2016). Ag-doped titanium dioxide gas sensor. In *IOP Conference Series: Materials Science and Engineering*, 108, (1–7).

[170] Lee, S. (2017). Electrodes for Semiconductor Gas Sensors. *Sensors*, 17(4) :1–19.

[171] Garner, W. E. and Reeves, L. W. (1954). The Thermal Decomposition of Silver Oxide. *Trans. Faraday Soc.*, 59: 254–260.

[172] Liu, K., Yan, P., Jiang, H., Xia Z., Z., Xu, Z., Bai, S. and Zhang, Z. C. (2019). Silver initiated hydrogen spillover on anatase TiO_2 creates active sites for selective hydrodeoxygenation of guaiacol. *J. Catal.*, 369: 396–404.

[173] Hazra, A., Das, S., Kanungo, J., Sarkar, C. K. and Basu, S. (2013). Studies on a resistive gas sensor based on sol – gel grown nanocrystalline p-TiO_2 thin film for fast hydrogen detection. *Sensors Actuators B. Chem.*, 183: 87–95.

[174] Radecka, M., Jasinski, M., Klich-Kafel, J., Rekas, M., Lyson, B., Czapla, A., Lubecka, M., Sokolowski, M., Zakrzewska, K., Heel, A. and Graule, T. J. (2010). TiO_2-based nanopowders for gas sensor. *Ceram. Mater.*, 64(4): 545–549.

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LIST OF PUBLICATIONS

Journals

S. Amaniah, M. Chachuli, M. N. Hamidon, M. S. Mamat, M. Ertugrul, and N. H. Abdullah, "A Hydrogen Gas Sensor Based on TiO_2 Nanoparticles on Alumina Substrate," Sensors, vol. 18, no. 2483, pp. 1–13, 2018.

S. A. Mohd Chachuli, M. N. Hamidon, M. S. Mamat, M. Ertugrulc, and N. H. Abdullah, "Response of TiO_2/MWCNT/B_2O_3 gas sensor to hydrogen using different organic binder," Mater. Sci. Semicond. Process. 99, 140–148, 2019.

Abdullah, N. H., Mustaffa, S., Nizar, M., Azis, S. & **Chachuli, S. A. M.**, "Structural transformations of mechanically alloyed polycrystalline $YMnO_3$-based material for gas sensing application," J. Aust. Ceram. Soc. 1–12, 2019.

Mohd Chachuli, S.A., Hamidon, M.N., Ertugrul, M., Mamat, M. S., Jaafar, H., Aris, Norhafiz, "Influence of B_2O_3 Addition on the Properties of TiO_2 Thick Film at Various Annealing Temperatures for Hydrogen Sensing," Journal of Elec. Materi, 2020).

Conferences

S. A. M. Chachuli, M. N. Hamidon, M. S. Mamat, and M. Ertugrul, "Detecting Hydrogen Using TiO_2-B_2O_3 at Different Operating Temperature," 2018 IEEE Int. Conf. Semicond. Electron., pp. 37–40, 2018.

S. A. M. Chachuli, M. N. Hamidon, M. S. Mamat, M. Ertugurul, and N. Abdullah, "Hydrogen Gas Sensing of TiO_2/MWCNT Thick Film via Screen-Printing Technique," *2019 IEEE Int. Conf. Sensors Nanotechnol.*, pp. 1–4, 2019.

S. A. M. Chachuli, M. N. Hamidon, M. Ertugrul, M. S. Mamat, H. Jaafar, and N. H. Shamsudin, "TiO_2/B_2O_3 Thick Film Gas Sensor for Monitoring Carbon Monoxide at Different Operating Temperatures," *J. Phys.: Conf. Ser.*, pp. 1-6, 2020.

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