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Ozone Sensing Properties of NbO₂ Thin Films for Health and Safety Applications

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Abstract—This work investigates the ozone sensing properties of NbO₂ thin films operating at room temperature. NbO₂ thin films have been deposited on alumina and glass substrates provide with Cu interdigitated electrodes by the Vacuum Thermal Evaporation technique. The optical properties of NbO₂ thin films were explored using CARY 1E UV-Visible Spectrophotometer. The values of the optical band gap E_{OPT} are estimated in view of the Mott and Davis' theory. The electrical response has been measured by exposing the sensing layers to ozone (ppb). NbO₂ films fabricated by this method have shown good sensitivity to environmentally relevant ozone concentrations.

Index Terms— Gas Sensor, Thin Film, Ozone, Niobium Oxide, Vacuum Thermal Evaporation

I. INTRODUCTION

Ozone is a strong clean oxidizing agent and is widely used as a disinfectant and deodorizing agent [1]. Ozone (O₃) has been classified as a dangerous pollutant by regulatory bodies around the world. Many electronic devices such as photocopiers and laser printers produce ozone. It has serious adverse effects on human health at extremely low concentrations; as a result the World Health Organization (WHO) has set exposure limits of 64 parts per billion (ppb) for up to 1hour exposure and as low as 43ppb for prolonged exposure (8 hours).

Ozone (O₃) measurement for air quality monitoring and atmospheric research is largely carried out by spectroscopic or electrochemical methods [1]. These techniques are very accurate and sensitive to atmospheric ozone concentrations but require expensive equipment as well as a high level of expertise for correct operation and subsequent data interpretation [2]. As ozone has very low allowable limits of < 100ppb, very high sensitivities and selectivity are required to avoid cross – interference with other oxidizing gases, such as, NO₂, SO₂, and Cl₂, which normally occur in higher concentrations [3].

Solid-state sensors have long been studied by several research groups [1], [2], [4], [5] and [6]. The strong interest evinced in this type of gas sensor is ascribed to its low production and operation costs compared to other types of sensors such as electrochemical cells and remote monitoring techniques [6]. Allied to these advantages are the simple design, robustness, fast response and the miniaturization of these devices [7].

Over the past 20 years, a great deal of research has been directed toward the development of small dimensional gas sensors for practical applications ranging from toxic gas detection to manufacturing process monitoring [3]. Such devices should allow continuous monitoring of the concentration of target gases in the environment in a quantitative and selective way [8]. However, many of these efforts have not reached commercial viability because of the problems associated with the sensor fabrication and the technologies applied to gas-sensing systems. With the increasing demand for better gas sensors of higher sensitivity and greater selectivity, intense efforts are being made find more suitable materials with the required surface and bulk properties for use in gas sensor devices [3].

Gas sensors based on metal oxide semiconductors have been the subject of many extensive investigations, primarily focusing on SnO₂. Using metal oxides has many advantages, such as simplicity in device structure, low cost of fabrication, robustness in practical applications, and adaptability to a wide variety of reductive and/or oxidative gases [3]. Thin film technology has not yet been introduced successfully in this group of gas sensors. Most of the commercially available sensors are basically of a sintered block or thick film type. There have been many attempts to utilize thin films for gas sensing applications. However, those attempts have barely been successful due to the physical shape of the thin films, mostly fabricated by dry processing methods, like RF sputtering, not being stable enough at the elevated temperatures required for sensor operation [3].

Most of the current metal oxide ozone gas sensors on the market operate at elevated temperatures (200°C – 600°C). The gas detection technique is primarily based on a change in the electrical resistance of the semiconducting metal oxide films.

The sensitivity and selectivity of metal oxide gas sensors is

dependent on operating temperature. Qu et al found that when operating the sensor at 200°C the sensitivity to 100 ppb of ozone was 1.4, while operating at 300°C the sensitivity of the device increased to 2.5 [10]. There is also the possibility of operating the sensor at two different temperatures to take advantage of the greater sensitivity achieved at lower temperatures (~400°C) and the faster response times which are achieved at the higher temperatures (~600°C) [10].

In addition to SnO₂, various other semiconducting metal oxides have been extensively investigated to gain a comprehensive understanding about the gas sensing mechanisms [9]. In₂O₃ and WO₃ are among the most widely investigated materials for the detection of strongly oxidizing gases, such as O₃ [1], [2], [4], [5], and [6].

Room temperature operation is a very desirable characteristic as it not only reduces fabrication and operating costs of the sensor, but also eases implementation into other portable/handheld devices.

Niobium oxide has been studied extensively due to its broad range of applications [11]. It is widely used in catalysts, gas sensors, electrochromic devices and optical fibres [12 - 15].

The detection principle of this material is based on the reversible modulation of the electrical conductance in the presence of oxidizing or reducing gases. Niobium oxide has been especially tested as an oxygen sensor where its conductivity decreases when oxygen partial pressure is increased [14].

Among the niobium oxides, Nb₂O₅, is gaining popularity for gas detection applications and is a very promising material for the development of integrated gas sensors. Table 1 shows a range of niobium oxide based gas sensors being utilized for various different target gases. Also illustrated are the sensors operating temperatures, which range from 20 – 750°C and the response time for each sensor.

II. SENSOR PREPARATION

The thin film structures were prepared using thermal deposition under high vacuum in an Edwards E306A coating system. The coating system is equipped with a 550 – Watt rotary pump and E040 diffusion pump capable of achieving a vacuum of 6.5×10^{-7} mbar with the assistance of a liquid nitrogen trap facility. The system also consists of an Edwards FTM5 quartz crystal monitor to read the rate of deposition and to measure the film thickness. The crystal was placed directly above the evaporation source and as close as possible to the substrate in order to obtain an accurate reading. The mass deposited on the crystal during the evaporation process alters its natural vibration frequency. Thus the monitor can record the rate of deposition and the thickness of the deposited layer corresponding to a frequency shift.

A. Interdigitated Structure (IDS)

Interdigitated structures (IDS) are commonly used as a basis for gas sensitive layers [24]. The advantage of sensors based on this structure is the simple and cheap fabrication process and the ability to use the sensor in a wide range of applications without crucial changes to the sensor design [25]. The IDS is an arrangement of two comb electrodes interlocked into each other. The structure can be considered as many resistors in parallel sandwiched between the substrate and the metal oxide sensing layer.

B. Electrode Preparation

For the electrical properties measurements, copper (Cu) electrodes were manufactured on the substrate via the thermal evaporation technique. Photoresist (Az5214) was then spin – coated onto the Cu layer (0 – 7000rpm) and allowed to cure in air for 24 hours before partial exposure to UV light to trace the desired electrode pattern. After the exposure the substrate was placed in a developer solution (Electrolube PDN250ML) for 20 – 30 seconds and then rinsed in the water and placed in the etching solution of SEMO 3207 fine etch crystals to reveal the interdigitated electrode pattern. In order to remove the remaining photoresist from the pattern the substrate was completely exposed to UV light and again in the developer solution for a further 20 – 30 seconds.

C. Sensing Layer

Deposition of the thin sensing layer was performed via the vacuum thermal evaporation technique. Niobium Oxide (NbO₂) was placed in a modified tungsten boat and heated under high vacuum conditions (6×10^{-7} mbar). Current was passed through the tungsten boat until the desired temperature (rate of deposition) was achieved. The vapour phase was condensed on the substrate, which was placed directly above the evaporation source. Once the desired thickness was reached the current flowing through the boat was switched off and the process was stopped. During evaporation the substrate was held constant at a temperature of 300°C. The sensing layer was deposited over the IDS structure in a rectangular pattern covering an area of 2mm x 3mm. The substrate was allowed to cool to room temperature before being exposed to atmospheric conditions.

TABLE I
 NIOBIUM OXIDE – BASED SENSORS

Niobium Oxide	Target Gas	Operating Temperature Range (C)	Range of Detection limits	Sensor Physical Parameter	Response Time	References
Nb ₂ O ₅	CO, NH ₃	450 – 500	100 – 1000 ppm	Electrical conductivity (IDS)	~ 3min	[16]
Nb ₂ O ₅	NH ₃	500	100 – 1000 ppm	Electrical conductivity (IDS)	~ 4min	[17]
Nb ₂ O ₅	C ₂ H ₅ OH	500	2.1 %	Electrical conductivity	< 1min	[18]
Nb ₂ O ₅	NH ₃ , CO	400 – 500	100 – 1000ppm	Electrical conductivity (IDS)	~ 4min	[19]
Nb ₂ O ₃	DMA, TMA, NH ₃	300 – 640	-	Electrical conductivity	-	[20]
Nb ₂ O ₅ doped with TiO ₂	Air/Fuel	550 – 750	0.01 – 100 kPa	Electrical conductivity	~ 5 min	[21]
Nb ₂ O ₅ doped with Pt/Pd/RuO ₂	Acetone	300	0.1 – 20 ppm	Electrical conductivity	~ 3 seconds	[22]
Nb ₂ O ₅ doped with SnO ₂	Ethanol, 1 – propanol, 1 – butanol	20	0.1 – 5 ppm and 0 – 100% RH	Electrical conductivity (IDS)	-	[23]

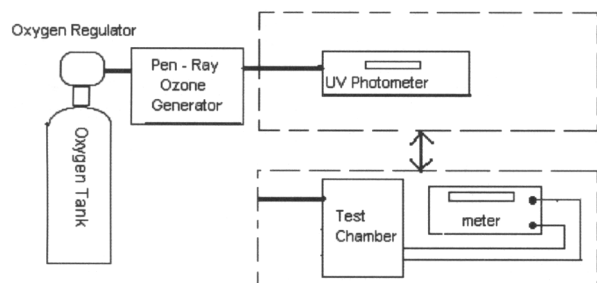


Figure 1. Basic Experimental Set-up

III. EXPERIMENTAL PROCEDURE

The sensors were tested in an in-house designed test rig. The test chamber consists of a Teflon base covered by a detachable Teflon structure containing inlet and outlet valves, allowing the target gas to flow directly over the sensing layer. Flow rate was controlled via a mass flow controller and during testing was held constant at a rate of 0.25l/min. The temperature inside the test chamber was held at room temperature.

Ozone was generated by pumping oxygen through a quartz tube under exposure from a pen – ray ultraviolet (UV) lamp (Ultra – Violet Products Ltd). Ozone concentration could be controlled by one of two ways, firstly by controlling the flow rate of oxygen through the quartz tube and secondly by adjusting a metal shutter enclosing the UV lamp, thereby

controlling the amount of UV being exposed. The Ozone concentration was calibrated with a UV analyzer (Ecosensors Ltd.). A thurlby multimeter was used to measure and record the variation in resistance of the sensor on exposure to ozone. Readings were automatically recorded every 30 seconds.

IV. RESULTS AND DISCUSSIONS

A. Optical Properties

The analysis of the optical absorption spectra has been one of the most important productive tools for understanding and developing the theory of the electronic structure of amorphous materials. In general, thin films prepared via the thermal evaporation technique are amorphous and at most they are polycrystalline in nature.

The optical energy gaps E_{OPT} for as-deposited and exposed to ozone films were determined from the high absorption regions of the fundamental edges using the Mott and Davis model [27]:

$$\alpha(\nu)h\nu = B(h\nu - E_{OPT})^n$$

where α is the absorption coefficient, E_{OPT} is the optical energy band gap, $h\nu$ is the energy of the incident photons,

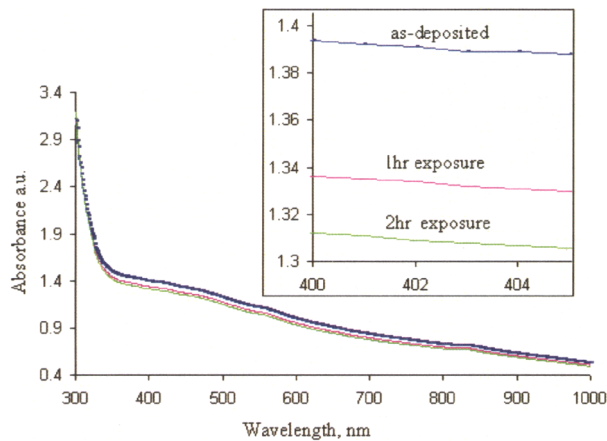


Figure 2. Plots of the optical absorbance spectra at UV-Vis wavelength range for 120nm of NbO₂ for as-deposited, 1hr and 2hr ozone exposure

and B is a constant. The exponent n of the energy dependence of the optical band gap can distinguish four cases of electronic transitions, which are summarized as follows: n = 1/2 for direct allowed transition, n = 3/2 for direct forbidden transition, n = 2 for indirect allowed transition and n = 3 for indirect forbidden transition [26].

Figure 2 shows the plots of the optical absorbance spectra at UV-Vis wavelength range for the thermally evaporated NbO₂ film: as-deposited and exposed to 3 ppm of ozone for 1 and 2 hours. It can be seen from Figure 2 that no appreciable changes in the optical properties were recorded in the wavelength range from 300 nm to approximately 340 nm. However, from 340 nm to 1000 nm the effect of ozone exposure manifested itself as a change in the optical density of the film. The greatest effect was seen after exposure for 1 hour, with the effect decreasing after continuing exposure, this effect could be clearly seen from the inset in Figure 2.

The change in the optical density is associated with the changes in the optical band gap, as can be seen from Figure 3. Using the Mott and Davis Theory [26], the estimated optical band gap for the as-deposited film was 3.66 and increased to around 3.68 after the film was exposed to ozone for 1 hour.

B. Sensor Performance

The principal detection process is the change of the oxygen concentration at the surface of these metal oxides, which is caused by the adsorption and heterogeneous catalytic reaction of oxidizing and reducing gaseous species [3]. There is a finite density of electron donors and/or acceptors bound to the surface of the semiconducting oxide. The electron donors/acceptors cause the formation of surface states followed by an exchange of electrons within the interior of the semiconductor thus forming a space charge layer close to the surface. By changing the surface concentration of the donors/acceptors, the conductance/resistance of the space charge region is modulated.

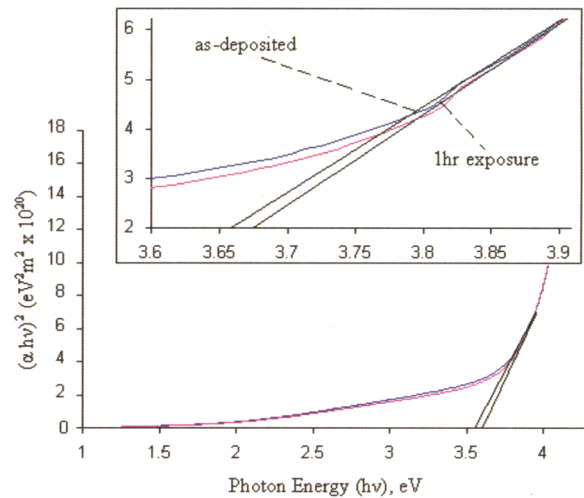


Figure 3. Plots of $(\alpha h\nu)^2$ versus photon energy $h\nu$ for as-deposited and exposed to ozone for 1 hour

If the oxide is an n-type there is a donation of electrons when reducing gases are introduced and a subtraction of electrons when oxidizing gases are introduced. The result is that n-type oxides increase their resistance when oxidizing gases are present and decrease resistance when reducing gases are present. In contrast to n-type, p-type oxides decrease resistance when oxidizing gases are present and increase resistance when reducing gases are present.

All the sensitivity results quoted were calculated using the following relationship: R_{TAR}/R_{REF} , where R_{TAR} was the measured resistance upon exposure to 240 ppb of ozone, and R_{REF} was the stable baseline resistance prior to ozone injection. Figure 4 illustrates the response of a 120nm-sensing layer deposited at a rate of 10-12nm/sec to environmentally relevant ozone concentrations (240ppb).

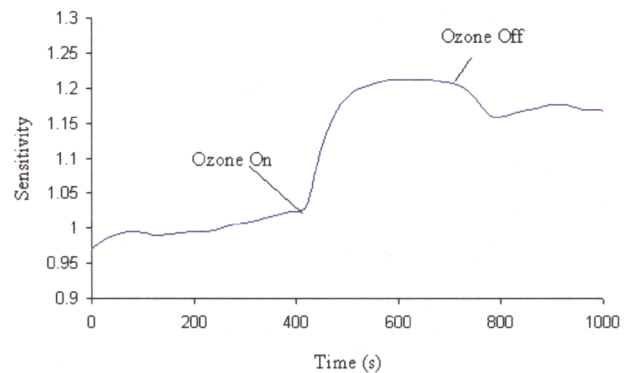


Figure 4. Response curve of 120nm NbO₂ sensing layer to 240ppb ozone

As can be seen from Figure 4 the sensor responds well to 240 ppb of ozone, however, the recovery of the sensor is poor, as it fails to return to a baseline resistance.

In general thin film sensors respond very easily towards strongly oxidizing gases [4]. This may be explained by the

geometry of the device, in a thin film sensor the outer sensor surface on which the interaction between the target gas and the sensing layer takes place and the actual current transport path between the electrodes beneath the sensing layer are very close together when compared to thick film devices.

Figure 5 illustrates the response of a 70 nm thick sensing layer deposited at a rate of 10-12nm/sec at a pressure of 5×10^{-6} mbar. As can be seen from Figures 4 and 5, the sensitivity of the device is greatly increased by reducing the thickness of the sensing layer. The sensitivity of the device increased from approximately 1.2 to 1.6, translating to a 30% increase in sensitivity.

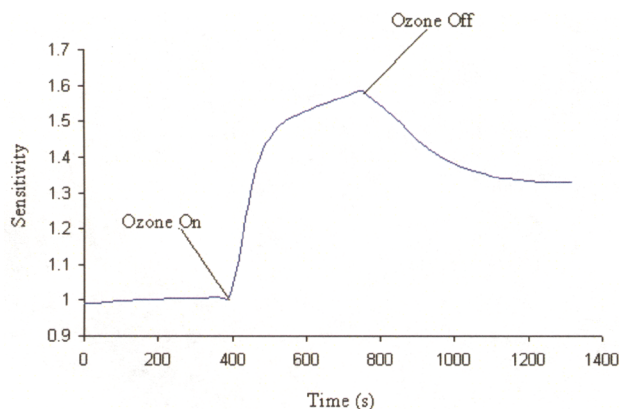


Figure 5. Response curve of 70nm NbO₂ sensing layer to 240ppb ozone

As can be seen from Figure 5 the recovery of the sensor is poor, however, previous work [27] has shown that careful control and selection of the fabrication parameters such as, deposition rate, layer thickness and material selection can yield a significant increase in sensor performance.

It is suggested that strongly oxidizing gases immediately interact with the outermost layers of the film, producing a resistivity change. Clearly, this effect will influence the conductance of a thin film device more than that of a thicker film [4].

Response time (T_{RES}) is calculated from Figures 4 and 5. It represents the time taken for the sensor to reach 90% of its final value after the target gas has been introduced. $T_{RES} = 75$ seconds for 70 nm and approximately 75 seconds for 120nm layer. Therefore, despite the increase in the sensitivity of the device for decreasing thickness, there is little or no change in the response time of the sensors.

V. CONCLUSIONS

This work has shown that thin films of NbO₂ are very promising for use as real-time environmentally relevant room temperature ozone sensors. Thin film devices were prepared using the Vacuum Thermal Evaporation (VTE) technique. It was found that depending on fabrication parameters that these thin films were sensitive to ozone concentrations in the ppb region.

Most of the current metal oxide based ozone sensors on the

market operate at elevated temperatures (>200°C) [2], [4], [5] and [6]. Room temperature operation offers many advantages over elevated temperature operation such as; reduced cost of fabrication, reduced power consumption and ease of implementation in to portable/handheld devices.

It is our intention to improve the overall sensor performance and further investigate the use of NbO₂ based thin films as reliable and accurate ozone sensors.

REFERENCES

- [1] G. Faglia, B. Allieri, E. Comini, L.E. Depero, L. Sangaletti, G. Sberveglieri, Electrical and structural properties of RGTO-In₂O₃ sensors for ozone detection, *Sensors and Actuators B* 57 (B) (1999) 188-191. W.-K. Chen, *Linear Networks and Systems* (Book style). Belmont, CA: Wadsworth, 1993, pp. 123-135.
- [2] C. Cantalini, W. Wlodarski, Y. Li, M. Passacantando, S. Santucci, E. Comini, G. Faglia, G. Sberveglieri, Investigation on the O₃ sensitivity properties of WO₃ thin films prepared by sol-gel, thermal evaporation and r.f. sputtering techniques, *Sensors and Actuators B* 64 (2000) pp. 182 - 188
- [3] G. Eranna, B.C. Joshi, D.P. Runthala, R.P. Gupta, "Oxide Materials for Development of integrated Gas Sensors – A Comprehensive Review", *Critical Reviews in Solid State and Materials Sciences* 29:3 (2004) 111 - 188.
- [4] T. Becker, L. Tomasi, C. Bosch-v.Braunmuhl, G. Muller, G. Sberveglieri, G. Fagli, E. Comini, Ozone detection using low-power-consumption metal-oxide gas sensors, *Sensors and Actuators* 74 (1999) 229-232
- [5] J. Frank, M. Fleischer, H. Meixner, A. Feltz, Enhancement of sensitivity and conductivity of semiconducting Ga₂O₃ gas sensors by doping with SnO₂, *Sensors and Actuators* 49 (B) (1998) 110-114.
- [6] S.R. Aliwell, J.F. Halsall, K.F.E. Pratt, J. O'Sullivan, R.L. Jones, Cox, Ozone Sensors based on WO₃: a model for sensor drift and a measurement correction method M. Young, *The Technical Writers Handbook*. Mill Valley, CA: University Science, 1989.
- [7] I.T. Weber, R. Andrade, E.R. Leite, E. Longo, "A study of the SnO₂-Nb₂O₅ system for an ethanol vapour sensor: a correlation between microstructure and sensor performance", *Sensors and Actuators B* 72 (2001) 180 - 183
- [8] M.S. Dutavie, R. Lalauze, C. Pijolat "Sintering, catalytic effects and defect chemistry in polycrystalline tin oxide", *Sensors and Actuators B* 26/27 (1995) 38 - 44
- [9] A. Mandeles, and C. Christofides, "Physics, Chemistry and Technology of Solid State Gas Sensor Devices", John Wiley & Sons, Inc., New York, 1993.
- [10] W. Qu, R. Green, and M. Austin, "Development of multi-functional sensors in thick-film and thin-film technology", *Measurement Science and Technology*, vol. 11, pp. 1111-1118, 2000G.
- [11] Y. Zhou, Z. Qiu, M. Lu, A. Zhang and Q.Ma, "Preparation and characterization of porous Nb₂O₅ nanoparticles", *Materials Research Bulletin*, MRB-3856, 2007.
- [12] I. Sieber, H. hildebrand, A. Fredrich and P. Schmuki, "Formation of self-organized niobium porous oxide on niobium", *Electrochemistry Communications*, 7, 97-100, 2005.
- [13] M. E. Gimon-Kinsel, K.J. Balkus, "Pulsed laser deposition of mesoporous niobium oxide thin films and application as chemical sensors", *Microporous and Mesoporous Materials*, 28, 113 - 123, 1999.
- [14] N. Ozer, D.G. Chen and C.M. Lambert, "Preparation and properties of spin-coated Nb₂O₅ films by the sol-gel process for electrochromic applications", *Thin Solid Films*, 277, 162 - 168, 1996
- [15] P. Viswanathamurthi, N. Bhattarai, H.Y. Kim, D. R. Lee, S. R. Kim and M.A. Morris, "Preparation and morphology of niobium oxide fibres by electrospinning", *Chemical Physics Letters*, 374, 79 - 84, 2003.
- [16] L. Chambon, J.P. Germain, A. Pauly, V. Demarne, and A. Grisel, "A Metallic Oxide Gas Sensor Array for a Selective Detection of Co an NH₃ Gases", *Sensors and Actuators B* 60, 138 - 147 (1999).

- [17] L. Chambon, C. Maleysson, A. Pauly, J.P. Germain, V. Demarne, and A. Grisel, "Investigation, for NH₃ Gas Sensing Applications, of the Nb₂O₅ Semiconductor Oxide in the presence of Interferent Species Such as Oxygen and Humidity", *Sensors and Actuators B* 45, 107 – 114 (1999)
- [18] T. Seiyama and S. Kagawa, "Study on a Detector for Gaseous Components using Semiconductive Thin Films", *Analytical Chemistry*, 38, 1069 – 1073 (1996).
- [19] L.Chambon, A. Pauly, J.P. Germain, C. Maleysson, V. Dermarne, and A. Grisel, "A Model for the Response of Nb₂O₅ Sensors to CO and NH₃ Gases", *Sensors and Actuators*, B43, 60 – 64, (1997)
- [20] M. Eagashira, Y. Shimizu, and Y. Takao, "Trimethylamine Sensor based on Semiconductive Metal Oxide for Detection of Fish Freshness", *Sensors and Actuators*, B1, 108 – 113, (1990).
- [21] J. Zhu, C. Ren, G. Chen, C. Yu, J. Wu, and H.Mu, "A New Automotive Air/Fuel Sensor Based on TiO₂ – Doped Nb₂O₅ Thin Film by Ion-Beam-Enhanced Deposition, *Sensors and Actuators*, B32, 209 – 213, (2001).
- [22] S.V. Ryabstev, A.V. Shaposhnick, A. N. Lukin, and E.P. Domashvskaya, "Application of Semiconductor Gas Sensors for Medical Diagnostics", *Sensors and Actuators* B59, 26 – 29, (1999)
- [23] B.P.J.d.L., Costello, R.j. Ewen, N.M. Ratcliffe, and P.S. Sivanand, "Thick Film Organic Vapour Sensors based on Binary Mixtures of Metal Oxides", *Sensors and Actuators*, B92, 159 – 166, (2003).
- [24] T. Hoffman, K. Schroder, J. Zacheja, J. Binder, "Fluid Characterisation using sensor elements based on interdigitated, electrodes", *Sensors and Actuators*, B37, 37 – 42, (1996).
- [25] M. Den Otter, "Approximate expressions for the capacitance and electrostatic potential of interdigitated electrodes", *Sensors and Actuators*, A96, 140 – 144, (2002).
- [26] N.F. Mott and E.A. Davis "Electronic Process in non – crystalline materials", Oxford, Uk, Clarendon Press, 1979.
- [27] O. Korostynska, K. Arshak, G. Hickey and E. Forde, "Ozone and gamma radiation sensing properties of In₂O₃:ZnO:SnO₂ thin films", *Microsystems Technologies*, (2007).