

IMPLEMENTATION OF MOX-SNO₂: ZNO NANO COMPOSITE SYNTHESIS AND COMSOL MULTIPHYSICS SIMULATION FOR TAGUCHI MEMS-VOC GAS BIOSENSORS.

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Abstract : Bio sensors are ruling the industry in the field of medical, health technology, gas sensing, environmental and vehicular technology, not only in the new era of Artificial Intelligence and Internet of things where chip-on data communications and remote monitoring of patient data outside hospital is possible. With the advent of MEMs and revolutionary changes in the NEMs fabrication methods and deposition techniques design of wearable bio sensors became trendy and favorable. Among the existing materials SnO₂:ZNO Nano composite materials are best suitable materials for the Gas sensing due to higher conductivity to oxidizing agents, lower adsorption to residual gases. Human exhale breathe analysis is required to estimate the voc compounds to detect the respiratory system diseases, detection or estimation of lung cancers. Simulations are carried using COMSOL Multiphysics on the other angle fabrication of bio sensors is carried out, Simulation results are mentioned and importance of bio-sensors is elevated by mentioning various Nano bio sensors device fabrication/deposition techniques. Material Synthesis methods are given in this paper to achieve the said above suitable applications.

IndexTerms - VoCs, biosensors, MoX sensors, Deposition techniques.

I. INTRODUCTION

Bio sensors are constructed with less than 1000 μm feature sizes with advent of MEMs it is possible. MEMs based bio-sensor for VOC estimation is mostly challenging aspect in terms of transducers, biological detection, environmental pollution detection, green house gases, chaos debris and e- waste pollution detection makes the human being lives safety and healthy monitoring. Micro-Nano Engineering techniques, signal processing systems which has to compute as fast as Human brain or at least with competence speed are mitigating in overall device performance. Miniaturization at component and device level at low power management with high I/O Density and high signal integrity, flawless designs with best packaging techniques are the leverages not only in medical/health technology but also in automotive, data communications, consumer and flexible electronic and photonic industries.

SAW gas sensor consists of a piezoelectric substrate materials among Quartz, lithium niobate, lithium tantalite materials, lithium niobate is patterned with an inter digitized electrodes (IDE) and a sensitive film like ZNO/SNO₂ Nano composites are deposited on top of the piezoelectric substrate that responds to a specific gas like acetone, methane, formaldehydes, VOCs. COMSOL Multiphysics5.4 based solutions, simulations and checked sensor performance parameters.

II.LITERATURE

Many researchers has come out with Nano composite material based gas sensors like SnO₂, WO₃, ZNO, Y₂O₃ materials as Nano wires, rods or powders form with best sensing performance. Yin.Mayao et.al showed that WO₃.SnO₂ Nano sheet composite with 2-step hydro thermal synthesis and sensing mechanism in which increase in response time with acetone sensing is less than 2s and best selectivity is observed for acetone exposed [6]. Nayak et.al [7] observed that with controlled size density of SnO₂ Nano particles and single step low temperature hydro thermal methods used to obtain best selectivity and sensitivity among the detection of ammonia, ethanol, acetone at various temperatures. Kida.etal [8] showed that heterogeneous interfaces or core size of hetero junction materials is the trends in gas sensing. Md.Zhan, Lorenz Ramaner et.al [9] evaluated performance of SnO₂ Nano wire gas sensors in terms of conductivity versus charge density at different diameters from 20-140nm a decrements in conductivity by increasing in charge density, smaller is Nano wire diameter steeper is the response observed. A higher selectivity, repeatably, and stability performance was studied with enhanced methane gas sensing of SNO₂ with Au Nano particle doped by impregnation method of hydro thermal synthesizing methods by Dong ping, Xue et.al[10]. Yan-Wong studied Nano flower structures with catalytic and spill-over effects of Au to achieve high stability and can detect up to 500ppm of methane and 6 times higher performance than that of pure SNO₂ and with MOS doping of noble metals like Au, Pd, Pt to pure SNO₂ improves gas sensing mechanism. MoX gas sensors by Nano structures given by Fatima surf studied n-type ZNO, Al doped ZNO and ZNO/MW CNT structures were extensively studied [3]. Abhishek Sharma, Sang-im yoo et.al compared sub solidus phase relation in Al₂O₃-SnO₂-Zn O compounds at 1200 °C in air with other ternary systems like In₂O₃-SnO₂-Zn O and Ga₂O₃-SnO₂-Zn O ternary compound structures.[1]. Sharma, A., Kim, D., & Yoo et.al observed Sub solidus phase relation in the semiconductor metal oxides with ternary compound structure of GeO₂-Zn O-SnO₂ system at 1100 °C in air.

III. SYNTHESIS METHODS

Synthesis of Nano composites are based on selection of materials i.e. semiconducting nature, metals, alloys, polymers, carbon based structures like CNT Single wall or Multi walls [12]. From the past decade synthesis processes are chosen as sol-gel, hydro thermal, combination of sol-thermal, mechano-chemical, high gravity reacting precipitating, Nano porous methods like two step process which includes hydro thermal and mixing of acetates to homo precipitation techniques and network structured nature by Solvo-Thermal method, high gravity reactive precipitation, heterogeneous co-precipitation and homogeneous co-precipitation methods are preferred synthesis methods [22]. Gas sensors Can be fabricated either of these following types based on materials chosen from the Periodic Table, Properties of materials, operating principle, fabrication and design structures and mechanical and electrical, optical, luminescence, photo catalysis properties and principles of operation as Ceramic based, Polymer based Sensors, Peizo Resistive, Capacitive type sensors, Pressure Sensors, Peizo electric, Semi conductive metal oxides, Metal oxide based Sensors(MoX), Acoustics, Alloy based, carbon based are known classifications over the past few decade [13]. Among all, MoX based gas sensors also named as Taguchi-gas sensors are preferred over Calorimetric, Organic and In-Organic sensors Optical, Electrochemical, Chemo resistive amperometric classes for the detection of volatile organic compounds (VoC) due to high sensitivity, broad sensing capability features in the range of ppm to ppb levels, over a wide range of minimal operating frequencies and low power requirements, low cost due to batch processing MEMs bio Sensors with Nano composite materials as sensing elements are required designs to make lab-on-chip, body on chip, flexi photonic on chip systems. The measurement technology has a tremendous growth in multivariate data analysis which has given a great lead to dynamic random data or information handling analysis. The raw response generated by the bio sensors are analyzed using various statistical and computational methods. Statistical methods such as Principle Component Analysis, CDA FW, CA, computational methods are Artificial Neural Networks, RBF. Choice of method depends on available data and type of results required. To find VOC concentrations with the availability of Instrumental the following Flame ionization detectors, (FID), Photo ionization detectors (PID), gas chromatography (GC), Mass spectroscopy (MS) or (GC -MS) are chosen to detect various gaseous environments and analyzed. [21].

IV. IMPLEMENTATION PROCESS FLOW

The VoC gas sensor design can be divided into 4 different categories named as Quadratic Stage Implementation as shown in fig[1].

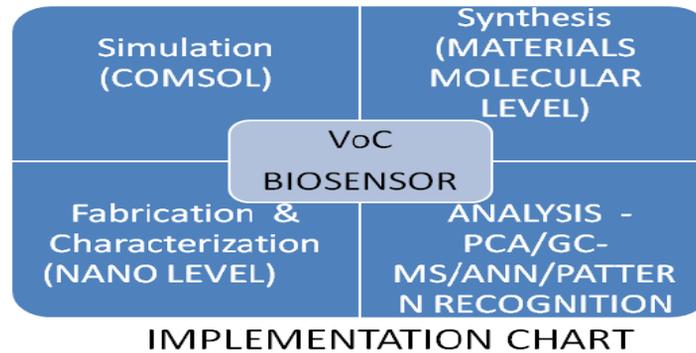


Fig [1]. Quadratic Stage Implementation Process flow of MoX based VoC BioSensor.

Classification of bio sensors based on transduction, transducer elements and bio reactive elements is represented as shown in following flowchart [2][13].

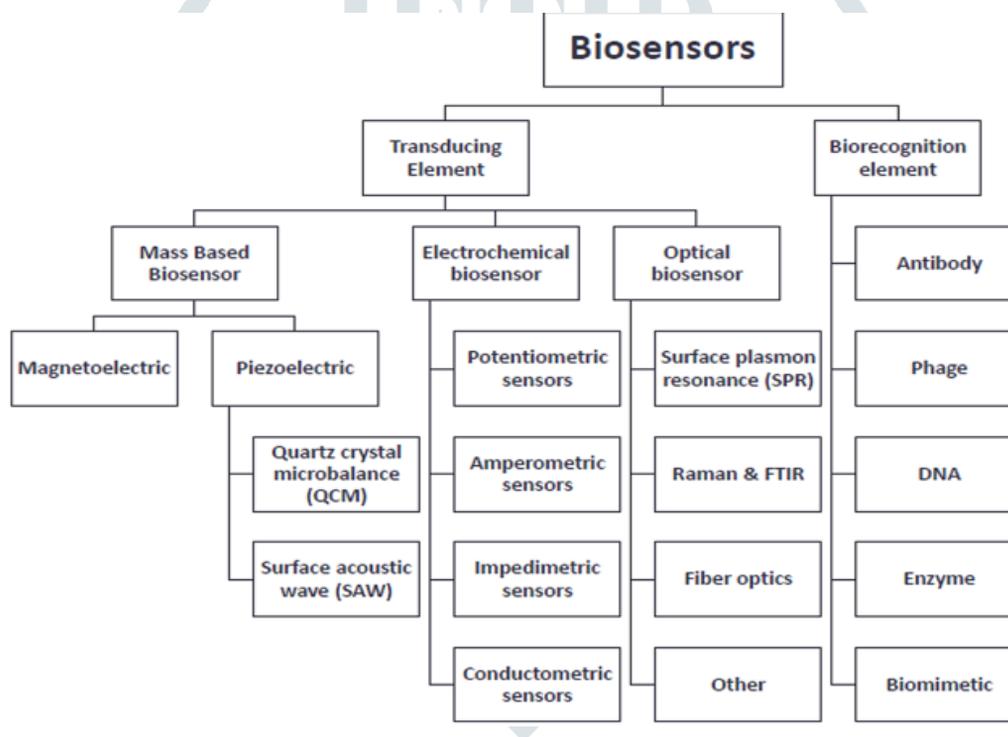


Fig [2]. Classification of MoX based VoC Bio-Sensors[13].

V. SYNTHESIS METHODOLOGY

In this present research paper a ZnO/SnO₂ Nano composite has been prepared by using single step Sol-Gel method. Chemicals considered are as listed all are AR grade.

1. Zinc chloride (ZnCl₂)M= 136.3g/mol >=95% pure- AR grade
2. Stannous or Tin chloride (SnCl₂) M=284.43g/mol with 99.99% pure- AR grade
3. Tri sodium Citrate as capping agent (C₆H₅Na₃O₇ . 2H₂O)
4. Sodium hydroxide (NaOH)-pellets
5. Ethanol
6. Distilled water

Step wise Reaction Procedure was mentioned clearly as follows

Step 1 : Aqueous Solution of Zinc chloride with 0.1 M of 13.63 g/m weighed and stannous chloride with 0.004 M with $M= 225.63\text{g/m}$ which is equal to 0.9025 g/m are taken, in two different beakers the above reactants are dissolve completely in 30ml+20ml of Distilled water respectively and it is stirred using magnetic stirrer, name it as solution -1.

Step 2 : Add a Capping agent: Tri sodium citrate $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ ---10mg of $M= 294.10$ to the solution -1. And name it as solution -2.

Step 3 : Sodium hydroxide (NaOH)-pellets 0.04M of 0.8 g weighed is dissolved completely in a 50 ml distilled water. And name it as solution -3

Step 4: Add this NaOH dissolved solution -3 to the Solution -2 slowly drop wise. Continue magnetic stirring for 3 hours.

Step 5: Observe that colourless solution changes in to milky white. After 3 hrs of stirring, flask was sealed for 6-10hrs.

Step6: A precipitate was suspended at the bottom of the beaker is collected by filtering, washed multiple times by ethanol and wash with distilled water and kept in a hot plate at 55°c - 85°c in the Hot Air Oven. A dried precipitate is collected as output.

Step :7 The collected sample is annealed and Sintered further at various temperatures @ 600°c , @ 700°c and @ 800°c for 2hours, using muffle furnace thereby purity can be enhanced and properties of the Nano composite material also be improved @ High temperatures.

Similarly the above steps are repeated with other molar Varied concentration of SnO_2 : 0.001M / ZNO 13.63g/m.The above steps from 1 to step7 are repeated at other molar concentration of SnCl_2 keeping ZN constant then annealed and Sintered samples to enhance nano composite properties.

Step :8 Aqueous Solution of Zinc chloride with 0.1 M of 13.63 g/m weighed and make a solution in 30ml of Distilled water and stannous chloride with 0.001 M with $M= 225.63\text{g/m}$ which is equal to 11.3 g/m in a 20ml DI water, these two are added until they dissolve completely by continuous stirring using magnetic stirrer, name it as solution -1. The above steps2 to Step-7 procedures were repeated for this second molar concentration too as shown figure[4].Then all the samples of 1st and 2nd composites which are collected from the muffle furnace are grinded thoroughly and separately for more than 30mins, then collected in to sample holders in the form of Nano powders output six samples are sent to XRD for further characterization.

VI. COMSOL MULTIPHYSICS SIMULATION RESULTS

The design structures of SAW gas sensor with tetrahedral meshing with fine and extremely fine configurations are simulated using COMSOL5.4 Multi physics through which surface pressure variations and min/max surface deformations with applied input pressures obtained are shown in the following figures shown [4-6] .

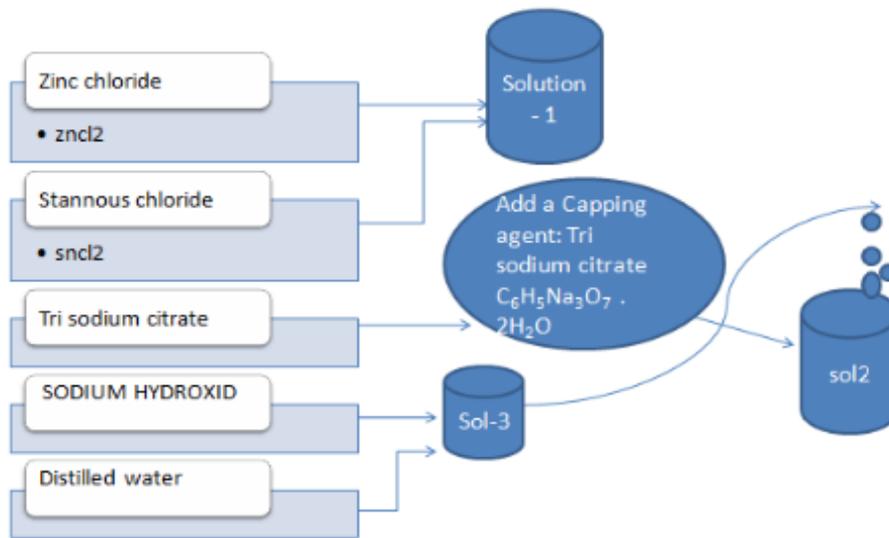
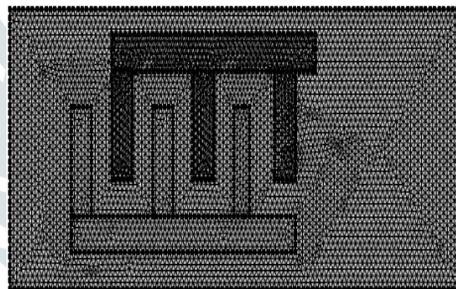


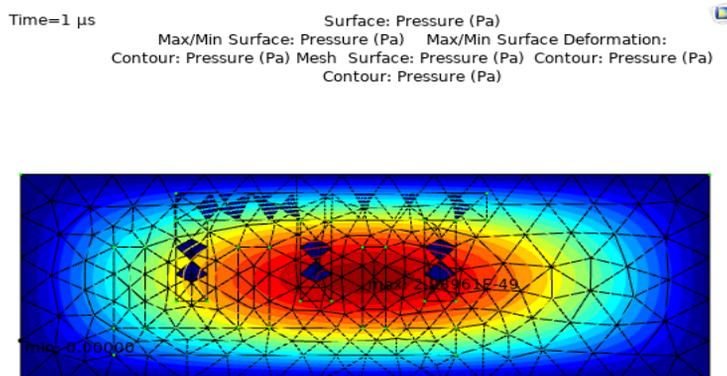
Fig [3]. Materials used for synthesis process of VOC Gas Bio Sensor

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Fig[4]. SAW gas sensor with tetrahedral meshing with extremely fine configurations.



Fig[5] . Surface Pressure Vs time contour

REFERENCES

- [1] Sharma. A & Yoo, S.-I. "Sub solidus phase relationships in the $\text{Al}_2\text{O}_3\text{-SnO}_2\text{-ZnO}$ ternary system at 1200 °C in air", *Journal of Alloys and Compounds*, 740, 536–540, 2018.
- [2] Sharma, A., Kim, D., & Yoo, S.-I. "Sub solidus phase diagram in the $\text{GeO}_2\text{-ZnO-SnO}_2$ system at 1100 °C in air. *Ceramics International*, 44(8), 9848-9853, 2018, doi: 5310.1016/j.ceramint.2018.02.228
- [3] Fatma Sarf "Metal Oxide Gas Sensors by Nanostructures" Physics Department, Çanakkale, Mart University, Çanakkale, web of science, Turkey DOI: 10.5772/intechopen.88858.
- [4] Blaschke, M., Tille, T., Robertson, P., Mair, S., Weimar, U., & Ulmer, H. (2006). "MEMS Gas-Sensor Array for Monitoring the Perceived Car-Cabin Air Quality", *IEEE Sensors Journal*, 6(5), 129-1308. doi:10.1109/jsen.2006.881399.
- [5] Suresh Kumar, Ravi Nigam et al "Sol-gel synthesis of ZnO–SnO₂ Nano composites and their morphological, structural and optical properties", Springer Science, *J Mater Sci: Mater Electron*, New York 2015, DOI 10.1007/s10854-015-2826-5.
- [6] Mingli Yin, Yao Yao, Haibo Fan, Shen Liu "WO₃-SnO₂ Nano sheet composites: Hydrothermal synthesis and gas sensing mechanism" *Journal of Alloys and Compounds*, Elsevier, 5 March 2018, doi 10.1016/j.jallcom.2017.11.185.
- [7] Arpan Kumar Nayak, Ruma Ghosh, Sumita Santra, Prasanta Kumar Guha and Debabrata Pradhan, "Hierarchical Nano structured WO₃-SnO₂ for selective sensing of volatile organic compounds" *Materials Science Centre, The Royal Society of chemistry, Nano scale*, 7, 12460–12473 Issue 29, 2015.
- [8] T. Kida, A. Nishiyama, Z. Hua, K. Suematsu, M. Yuasa and K. Shimano, "WO₃ Nano lamella Gas Sensor: Porosity Control Using SnO₂ Nanoparticles for Enhanced NO₂ Sensing", *Langmuir*, 2014, 30, 2571–257.
- [9] Md. Zhian, Anton kok et al "Response modeling of single SnO₂ nanowire gas sensors", *Sensors and Actuators B: Chemical*, Elsevier, Vol: 15, 22-29. September 2019.
- [10] Degong Ding, Q. Zhong Xue, Yonggan Du, Ya Xiong, J. Zhang, Xinglong Pan, "Great enhancement of CH₄ sensitivity of SnO₂ based Nano fibers by heterogeneous sensitization and catalytic effect" *Sensors and Actuators B: Chemical*, Volume 254, January 2018, 393-401 Doi. 10.1016/j.snb.2017.07.128.
- [11] Pedro Henrique Cury Camargo, Kestur Gundappa Satyanarayana, Fernando Wypych "Nanocomposites: Synthesis, Structure, Properties and New Application Opportunities" 81531-990 Curitiba - PR, Brazil, February 10, 2009.
- [12] www.mdpi.com/biosensors/biosensor40472/article_deploy/html/images/biosensors-04-00472-g004-1024.
- [13] Xiaohua Jia, Huiqing Fan, Lei Qin & Chao Yang, "Hierarchically Structure SnO₂/ZnO Nanocomposites: Preparation, Growth Mechanism and Gas Sensing Property", *Journal of Dispersion Science and Technology*, 31:10, 1405-1408.
- [14] Suresh Kumar, Ravi Nigam, Virender Kundu, Neena Jaggi, "Sol-gel synthesis of ZnO–SnO₂ Nanocomposites and their morphological, structural and optical properties" Received: 11 December 2014 / Accepted: *J Mater Science: Mater Electron Springer Science*, New York, 6 February 2015. doi:10.1007/s10854-015-2826-5.
- [15] Pakhare, K.S., Sargar, B.M., Potdar, S.S. Potdar et al, "Facile Synthesis of Nano-Diced SnO₂-ZnO Composite by Chemical Route for Gas Sensor Application," *Journal of Electronic Materials*, 48, 669–6279 2019, doi: 10.1007/s11664-019-07419-9.
- [16] Gu, F., Wang, S. F., Lü, M. K., Zhou, G. J., Xu, D., & Yuan, D. R. "Photoluminescence Properties of SnO₂ Nanoparticles Synthesized by Sol-Gel Method" *The Journal of Physical Chemistry B*, 108(24), 2004, 8119–8123. doi:10.1021/jp036741e.
- [17] Sekhar, D. C., Diwakar, B. S., & Madhavi, N. "Synthesis, characterization and anti-bacterial screening of complex Nanocomposites structures of SiO₂@ZnO@Fe₃O₄ and SnO₂@ZnO@Fe₃O₄ NanoStructures & Nanoobjects, 100374, doi:10.1016 /j.nanoso.2019.

- [18]Chiu, H.-C., & Yeh, C.-S. (2007) “Hydrothermal Synthesis of SnO₂ Nanoparticles and Their Gas-Sensing of Alcohol”, The Journal of Physical Chemistry C, 111(20), 7256–7259. doi:10.1021/jp0688355.
- [19]Jiang, L., Sun, G., Zhou, Z., Sun, S., Wang, Q., Yan, S.Xin, Q. “Size-Controllable Synthesis of Monodispersed SnO₂Nanoparticles and Application in Electrocatalysts”. The Journal of Physical Chemistry B, 109(18), 8774–8778. (2005). doi:10.1021/jp050334g
- [20]Yude, W., Shuo, Z., Xinghui, W., & Qingju, L. “Synthesis and optical properties of Nano-ZnO particles/meso structured SnO₂ composite”, Materials Chemistry and Physics,98(1),12124. doi:10.1016/j.matchemphys.2005.08.074.
- [21]Daniel Ruffer, Felix Hoehne and Johannes Buhler, “New Digital Metal-Oxide (MOX) Sensor Platform”, Sensors 18(4), 1052,31 March 2018,doi. 10.3390/s1804105.
- [22] A. Hamrouni, N. Moussa, F. Parrino, A. Di Paola, A. Houas, L. Palmisano, “Sol-gel synthesis and photo catalytic activity of ZnOSnO₂ Nano composites”, Journal of Molecular Catalysis A: Chemical (2014), <http://dx.doi.org/10.1016/j.molcata.2014.03.018>.

