iJRASET
International Journal For Research in Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 9 **Issue:** II **Month of publication:** February 2021

DOI: https://doi.org/10.22214/ijraset.2021.32980

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.429
Volume 9 Issue II Feb 2021- Available at www.ijraset.com

Zn_2SnO_4 Modified ZnO Thick Film Resistors as LPG Sensor

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Abstract: ***Zinc oxide nanostructures were synthesized by chemical route method. The XRD spectrum indicates that the sample is wurtezite (hexagonal) structured ZnO with lattice constants of a = 3.249A^0, c = 5.206 A^0. Thick films of synthesized ZnO were prepared by screen printing technique. The Zn_2SnO_4 modified ZnO were obtained by dipping them into an aqueous solution of $SnCl_4.5H_2O$ for different interval of time. Gas sensing properties of pure and modified ZnO thick films were investigated. The Zn_2SnO_4 modified ZnO thick film dipped for 3 min was observed to be more sensitive to LPG at 240^{0}C as compared to other modified thick films. The effect of surface microstructure and Zn_2SnO_4 concentration on the sensitivity, selectivity, response and recovery of the sensor in the presence of LPG were studied and discussed.***

Keywords: ZnO nanostructure, Zn_2SnO_4 modified ZnO thick films, LPG Sensor.

I. INTRODUCTION

The detection of toxic and inflammable gases by a sensor was extremely important for human and environmental protection. Research on the gas sensors was aimed to obtaining new sensing materials to achieve highly sensitive and selective devices. ZnO has proven to be highly sensitive materials for the detection of both reducing and oxidizing gases [1-10]. Though, poor selectivity is one of its disadvantages.

Semiconductor gas sensors based on SnO_2 and ZnO have been studied for the detection of toxic or inflammable gases [11-14]. However, high operating temperature is one of their disadvantages. In order to modify the gas sensing properties, the use of metal additives such as Ag, Pt and Pd as catalysts were widely studied [15]. Another approach was the utilization of the interfaces between two different oxides such as hetero contact of p-n junction with new sensing mechanism was proposed to improve its sensing properties. However, the hetero contact type sensors have the poor reliability due to its pressed contact [16]. Composite type sensors were suggested to improve the reliability since they contain many heterogeneous interfaces between different phases. However, the composites make the study of the individual interface difficult. To overcome these problems, only surface of metal oxides were modified with other oxides by using dipping technology. In present work, the efforts were made to modify surface of ZnO nanostructure thick film with Zn_2SnO_4 crystals by using dipping technique to improve sensing properties.

II. EXPERIMENTAL

A. Synthesis of ZnO nanostructure

All chemicals were of analytical grade and used as purchased without further purification.

In present work, 2.974 g Zinc nitrate hexahydrate was dissolved in 100 ml distilled water and 2.0g of NaoH was dissolved in 100 ml distilled water. The zinc nitrate solution was added drop wise to the NaoH solution to form white solution. Then, white solution was subsequently kept at 75^{0}C for 12h. The resulting white precipitates were collected by centrifugation, washed with distilled water and ethanol several times and then dried at 80^{0}C in vacuum oven for 2h. The synthesized ZnO nanostructure was used for further study.

B. Preparation of thick films

Thick films of ZnO nanostructure were prepared by using screen printing technique. In present process, paste was formulated by mixing the ZnO nanostructure powder with ethyl cellulose in a mixture of organic solvents. The ratio of ZnO to ethyl cellulose was kept 93:07. The paste was screen printed on a glass substrate in desired patterns. The films were fired at 500^{0}C for 2h to remove temporary binder. Prepared thick films termed as pure ZnO thick films.

C. Zn_2SnO_4 Modified ZnO thick Films

Surface of pure ZnO thick film were modified by dipping them into a 0.01 M aqueous solution of $SnCl_4.5H_2O$ for different intervals of time (1, 3, 5 & 7 min). After dipping, thick films were dried under IR lamp for 45 min. and calcinated at 700^{0}C for 4h in air ambient. In calcination process, tin chlorides dispersed on the film surface were reacting with surface ZnO molecules and oxidized. Therefore sensor elements with different mass% of Zn_2SnO_4 on the surface of ZnO thick film were obtained. These surface activated films are termed as Zn_2SnO_4 modified thick films.

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D. Characterization

The synthesized ZnO were characterized for structure and morphology by power X-ray diffraction (Philips PW 1710) and transmission electron microscopy (TecnaiG2 20 ultra-twin). The microstructure and chemical composition of the films were analyzed using a field emission scanning electron microscope (ZEISS SUPRA-55) coupled with an energy dispersive spectrometer. Thickness measurements were carried out using Marutek film Thickness Measurement System. Gas sensing characteristics were measured using a static gas sensing system.

E. Static Gas Sensing System

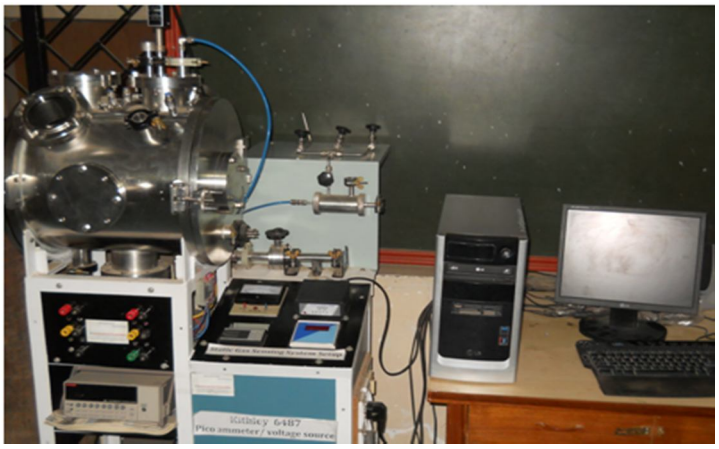


Fig. 1 Photograph of computerized gas sensing system

Fig. 1 represents photograph of computerized static gas sensing system to examine the sensing performance of the thick films. A constant voltage was applied to the sensor element and current was measured with the help of voltage source cum picoammeter (Keithley 6487). Heating element and thermocouple were connected to temperature controller (Nippon NC 2638). Sensor element and thermocouple were kept on the insulating surface of the heating element. The required gas concentration inside the static system was achieved by injecting a known volume of test gas using a syringe. The vacuum pump is attached to chamber to create vacuum or to remove test gas.

III. MATERIAL CHARACTERIZATION:

A. X-ray Diffraction

The recorded X-ray diffraction pattern (Fig. 2) confirmed that synthesized ZnO is highly crystalline in nature. The corresponding X-ray diffraction peak for (100), (002), (101) and (102) planes confirm the formation of hexagonal wurtzite structure of ZnO, which are in good agreement with the literature values (JCPDS card No. 36-1451). In this X-ray diffraction pattern, extra pick appear at $2\theta = 44^0$. This peak was identified as surface hydroxyl groups, which can be related to the formation of water on the ZnO nanostructure surface [17]. The crystallite size was calculated by using Scherrer's formula [18] and found to be 16nm.

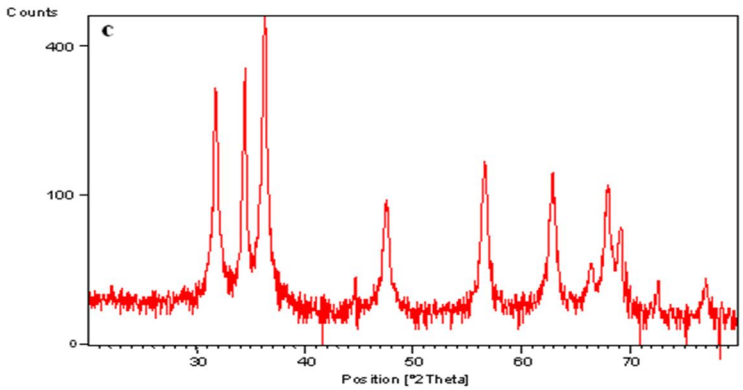


Fig. 2 powder XRD pattern of ZnO nanostructure synthesized by chemical route method

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B. Transmission electron Microscope

Fig.3 illustrates the TEM image of the ZnO nanoparticles. TEM pattern shows that the particles are agglomerated up to some extent.

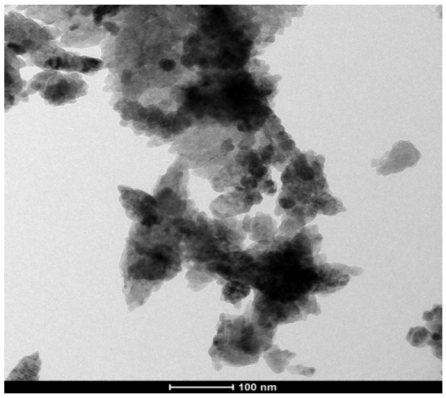


Fig. 3 TEM image of ZnO nanostructure synthesized by chemical route method

C. Scanning Electron Microscope

The FE-SEM micrograph of the pure ZnO thick film prepared by screen printing technique is shown in Fig. 4a. Pure ZnO thick film consists of randomly distributed nanosheets. Fig. 4b corresponds to surface modified ZnO thick film with dipping time 1 min, clearly indicate that, growth of nanosize octahedral crystal began to occur on the surface of ZnO thick films. These nanosize octahedral crystals attributed to Zn_2SnO_4. Thus effective surface area of thick film gets increased. As dipping time increases to 3 min, growth of more and more Zn_2SnO_4 crystals on the surface of ZnO thick films occur (Fig. 4c). Further increasing in dipping time to 5min and 7min, these nanoscale Zn_2SnO_4 crystals start to disperse core of ZnO nanostructure as shown in Fig. 4d and 4e respectively. Fig. 4f shows high magnified FE-SEM image of Zn_2SnO_4 crystal created on the surface of modified ZnO thick film (dipped for 3 min.).

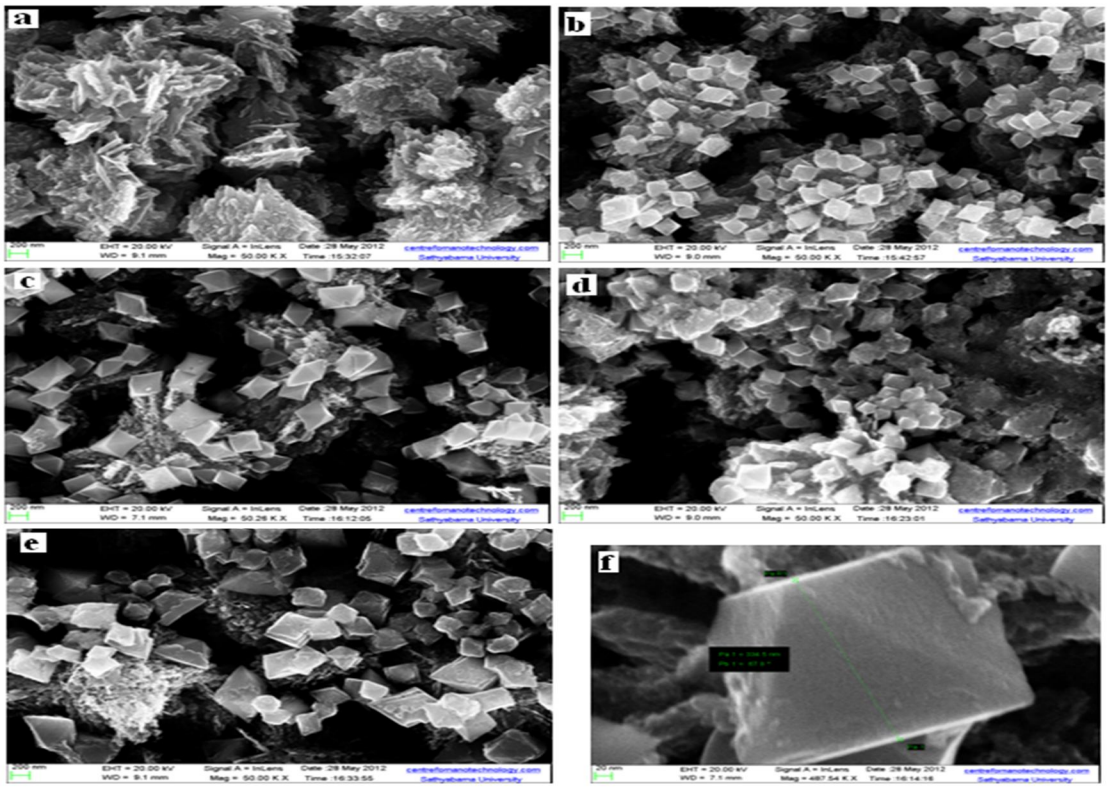


Fig. 4 FE-SEM images of **a)** pure ZnO thick film & modified ZnO thick film **b)** dipped for 1 min. **c)** dipped for 3 min. **d)** dipped for 5 min. **e)** dipped for 7 min. **f)** Highly magnified modified ZnO thick film (3 min dip.)

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D. Elemental Analysis

Fig. 5a-e represents the EDS patterns of pure and modified ZnO Thick films. These Figures illustrate that as the dipping time increases intensity of tin peak increases, which indicate the increasing in mass percentage of tin element on the surface of the ZnO thick film.

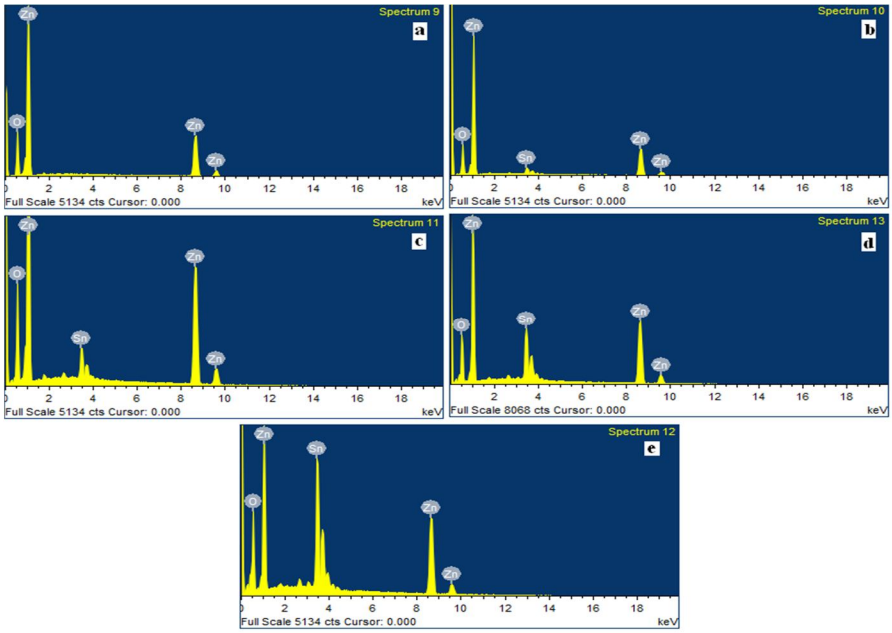


Fig. 5 EDS patterns of **a)** pure ZnO thick film & modified ZnO thick film **b)** dipped for 1 min. **c)** dipped for 3 min. **d)** dipped for 5 min. **e)** dipped for 7 min.

IV. SENSING PERFORMANCE

A. Pure ZnO thick film

The gas response of the sensor was defied as the ratio of the change in conductance of a sample upon exposure to the target gas to the original conductance in air. The variation of gas response of ZnO thick film to 600ppm LPG with operating temperature is represented in Fig. 6. The response to LPG increases with increasing the operating temperature, reaches to the maximum (6.7) at 300^0C and decreases with further increasing operating temperature. Response to a gas is due to the interaction between hydrocarbons (propane and butane present in LPG) and adsorbed oxygen ions present on the surface of the thick film. When hydrocarbons interact with the adsorbed oxygen ions on the surface of ZnO thick film they are converted to CO_2 and H_2O and releases the trapped electrons back to the conduction band of the zinc oxide thick film. As a result the conductance of ZnO thick film increases in existence of LPG.

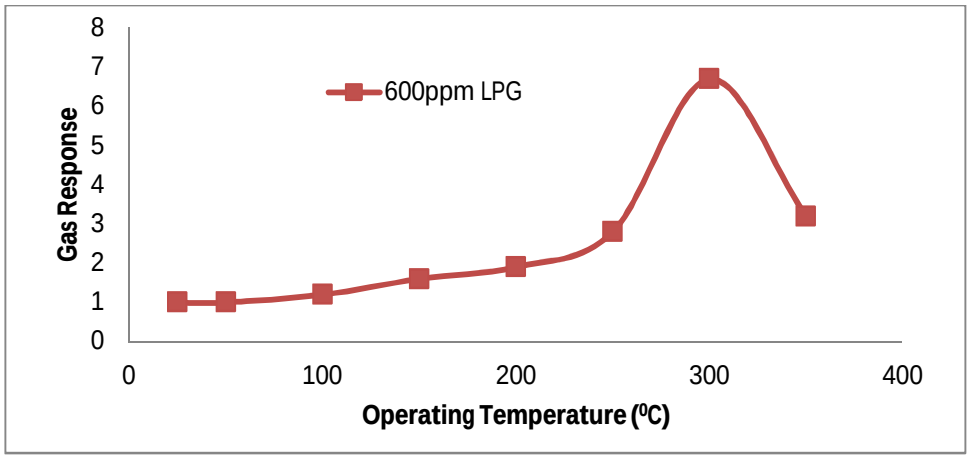


Fig. 6 variation of gas response of pure ZnO thick film with temperature

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B. Zn2SnO4 modified ZnO thick films

1) *Gas response and Operating Temperature:* The variation of gas response of modified ZnO thick films to LPG as a function of operating temperature is shown in Fig. 7. It represent that modified ZnO thick films with different dipping time are sensitive to 600 ppm LPG in the temperature range 200-300^{0}C. The highest response of all thick films was observed around temperature 250^{0}C.

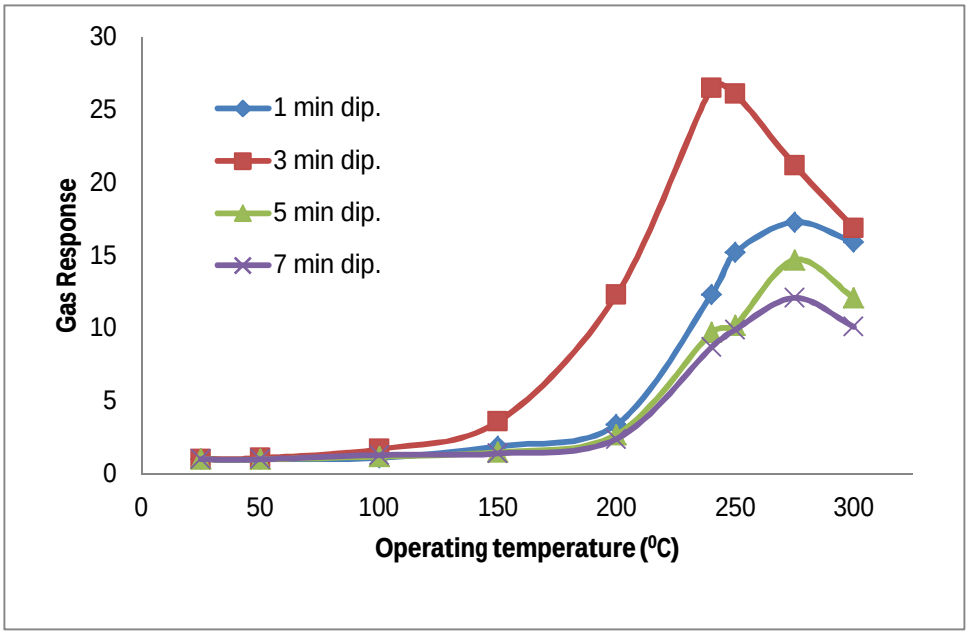
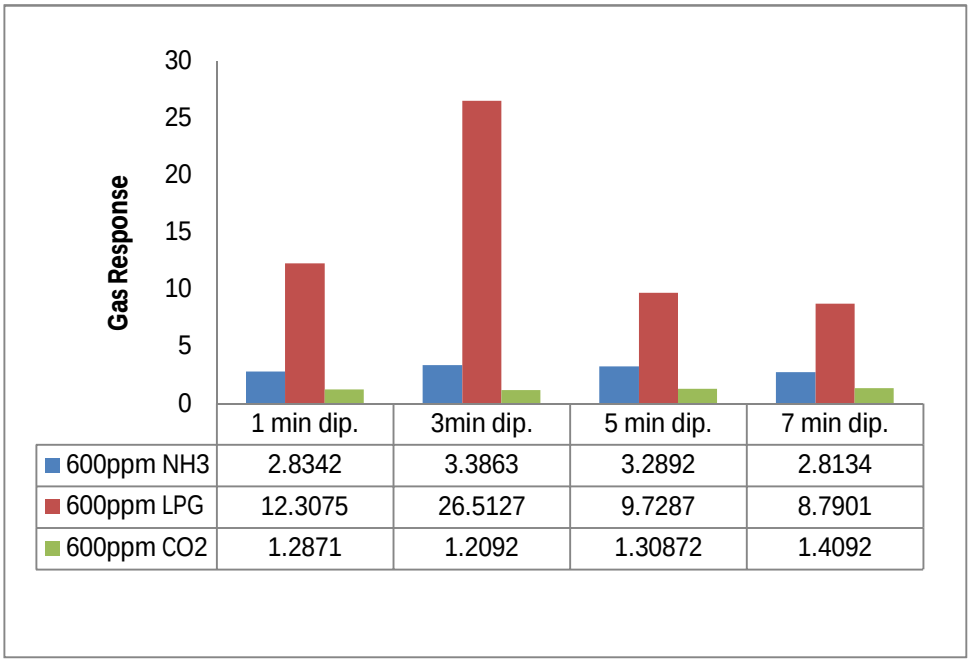


Fig. 7 variation of gas response of modified ZnO thick films with operating temperature.

2) *Selectivity for LPG Against Various Gases*



	1 min dip.	3min dip.	5 min dip.	7 min dip.
600ppm NH3	2.8342	3.3863	3.2892	2.8134
600ppm LPG	12.3075	26.5127	9.7287	8.7901
600ppm CO2	1.2871	1.2092	1.30872	1.4092

Fig. 8 Selectivity of modified ZnO thick films to LPG from mixture of gases at operating temperature 240^{0}C.

Fig. 8 demonstrate the selectivity of all modified ZnO thick films for 600 ppm LPG, NH_3 and CO_2 gas at operating temperature 240^{0}C. These modified thick films showed high selectivity to LPG among the gases such as CO_2 and NH_3.

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3) Response and Recovery time of the Sensor: Fig. 9 illustrates the response and recovery of the modified ZnO thick (3 min dip). It indicates that the response was quick (6 s) to 600 ppm of LPG, while the recovery is also fast (8 s) at operating temperature 240^0C.

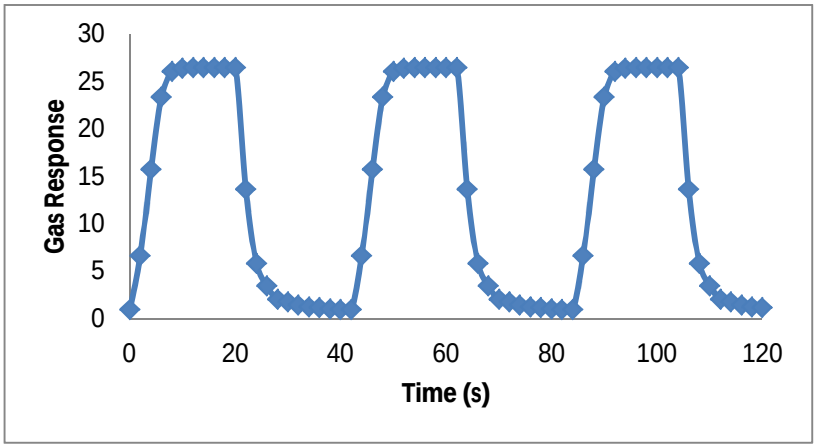


Fig. 9 variation of gas response of modified ZnO thick film (dipped for 3 min) to 600ppm LPG with time

All modified ZnO thick films gives quick response to LPG at higher operating temperature and fast recovery when sensor element keeps in air atmosphere. Such quick response and fast recovery can be explained on basis of adsorption and desorption process of oxygen ions on surface of Zn_2SnO_4 modified ZnO thick film.

V. DISCUSSION

Enhancement of sensing performance of Zn_2SnO_4 modified ZnO thick film to LPG [Fig. 7] as compared to pure ZnO thick films [Fig. 6] can be attributed to growth of zinc stanate crystals on the surface of ZnO thick film. This will increase the surface to volume ratio of the sensor material. The chemical composition and crystal morphology of Zn_2SnO_4 offers enhanced active sites for reactions of LPG molecules with adsorbed oxygen.

When Zn_2SnO_4 modified thick film exposed to air, oxygen molecules were adsorbed on the Zn_2SnO_4 surface, which generate ionized oxygen species by trapping electrons from the conductance band of Zn_2SnO_4. These generated ionized oxygen species react with reducing gas such a LPG, which resulted in the release of electrons to the surface of Zn_2SnO_4 modified ZnO thick film. Thus the conductivity of Zn_2SnO_4 modified ZnO thick films were increases gradually.

Fig. 7 shows that the sensitivity of Zn_2SnO_4 modified ZnO thick film (dipped for 3 min) is highest among other thick films in the temperature region 200-300^0C, it may be attributed to morphology of Zn_2SnO_4 crystals developed on the surface of ZnO thick film. The adsorption and desorption processes, which determine the sensor response mainly depends on the orientation and morphology of the crystals.

As the size of the crystal domain becomes smaller, the ratio of edge and corner atoms increases and also the surface topology becomes increasingly roughened [19]. Control of crystal size distributions and resulting changes in electronic and surface states provides an opportunity to tailor the interaction and adsorption of gas molecules on the exposed surfaces of Zn_2SnO_4 cubic structures and ZnO nanostructure resulting in enhanced sensor performance.

VI. SUMMARY

The sensing performance of pure and modified ZnO thick films can be summarized as

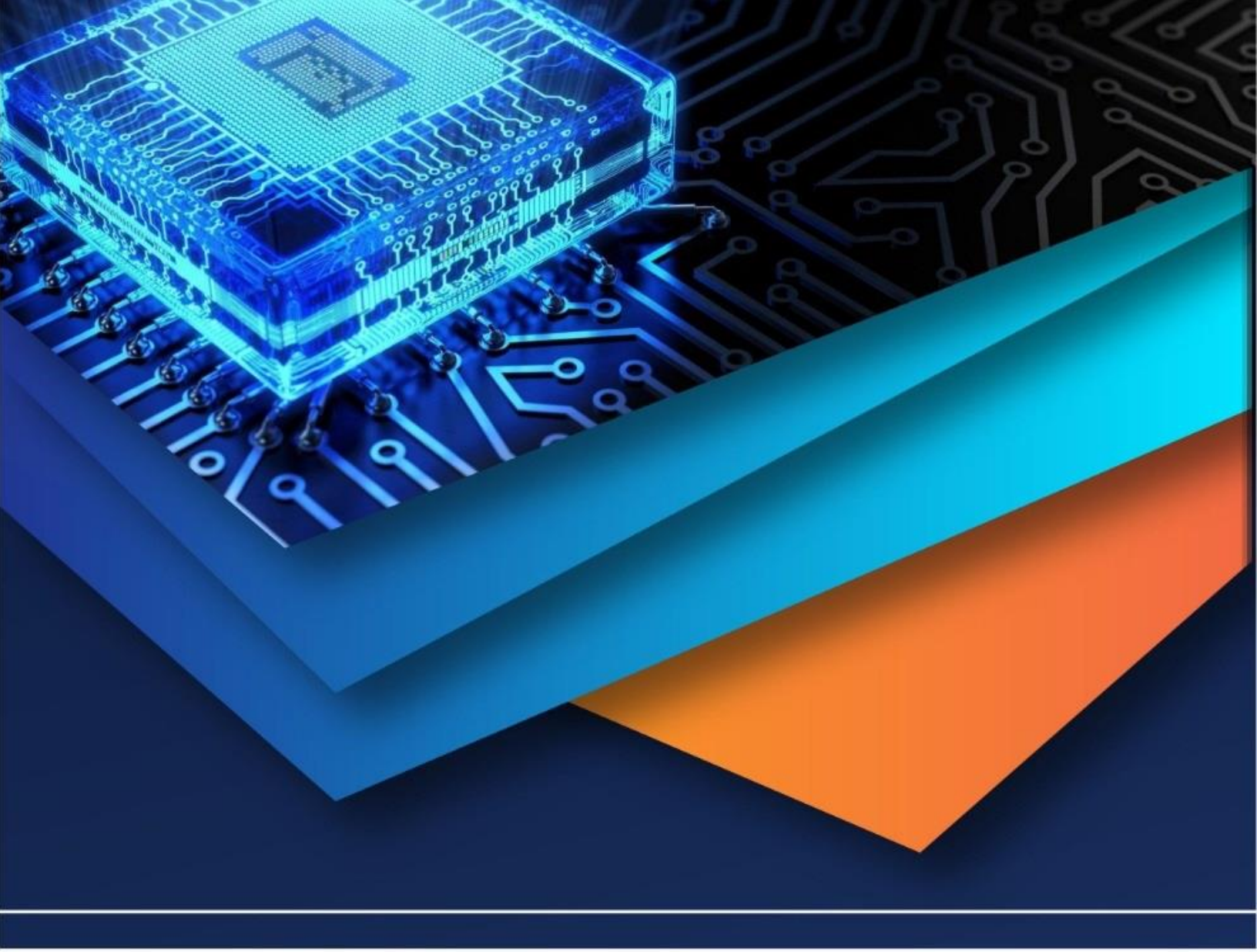
A. Zinc oxide power synthesized by chemical route method consists of nanoparticles and nanorods.
B. Pure ZnO thick films showed higher sensitivity and selectivity to 600 ppm LPG gas at 300^0C.
C. In case of surface modified thick films, thick film (dipped for 7 min.) shows higher conductivity.
D. All modified ZnO thick films shows sensitive to 600ppm of LPG in the temperature range 200-300^0C.
E. At 240^0C, modified ZnO thick film (dipped for 3 min.) shows higher sensitivity to 600 ppm of LPG as compared to other modified ZnO thick films.
F. Modified ZnO thick films showed very rapid response and fast recovery as compared to pure ZnO thick films.

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REFERENCES

[1] V. R. Shinde, T. P. Gujar, and C. D. Lokhande, LPG sensing properties of ZnO films prepared by spray pyrolysis method: effect of molarity of precursor solution, Sens. Actuators B 120 (2007) 551–559.
[2] T. J. Hsueh, Y. W. Chen, S. J. Chang, S. F. Wang, C. L. Hsu, Y. R. Lin, T. S. Lin, I. C. Chen, ZnO nanowire-based CO sensors prepared on patterned ZnO: Ga / SiO_2 / Si templates, Sens. Actuators B 125 (2007) 498-503.
[3]
[4] L. Chaikarn, P. Sukon, Influence of thickness on ethanol sensing characteristics of doctor-bladed thick film form flame-made ZnO nanoparticles, Sensors 7 (2007) 185-201.
[5] P. Mitra, A. Halder, Effect of initialization time on application potentiality of a ZnO thin film based LPG sensor, Mat. Res. 12 (2009) 329-332
[6] D. R. Patil, L. A. Patil, Preparation and study of NH3 gas sensing behavior of Fe2O3 doped ZnO thick film resistors, Sens. Transducers 70 (2006) 661- 670.
[7] D. R. Patil, L. A. Patil, P. P. Patil, Cr_2O_3 activated ZnO thick film resistors for ammonia gas sensing operable at room temperature, Sens. Actuators B 126 (2007) 368–374.
[8] G. S. Trivikrama Rao, D. Tarakarama Rao, Gas sensitivity of ZnO based thick film sensor to NH_3 at room temperature, Sens. Actuators B 55 (1999) 166–169
[9] O. Lupan, L. Chow, S. Shishiyanu, E. Monaico, T. Shishiyanu, V. Sontea, B. Roldan Cuenya, A. Naitabdi, S. Park, A. Schulte, Nanostructured zinc oxide films synthesized by successive chemical solution deposition for gas sensor applications, Mat. Res. Bull. 44 (2009) 63–69
[10] K.V. Gurav, U.M. Patil, S.W. Shin, S.M. Pawar, J.H. Kim, C.D. Lokhande, Morphology evolution of ZnO thin films from aqueous solutions and their application to liquefied petroleum gas (LPG) sensor, J. Alloy. Comp., 525 (2012) 1-7.
[11] S. Mondal, K. P. Kanta, P. Mitra, Preparation of Al-doped ZnO thin film by SILAR, J. Phys. Sci. 12 (2008) 221-229.
[12] W. H. Zhang, W. D. Zhang, Fabrication of SnO_2–ZnO nanocomposite sensor for selective sensing of trimethylamine and the freshness of fishes, Sens. Actuators B 134 (2008) 403-408.
[13] X. Song, L. Liu, Characterization of electrospun ZnO-SnO2 nanofibers for ethanol sensor, Sens. Actuators A 154 (2009) 175–179
[14] K. Won Kim, P. S. Cho, S. J. Kim, J. H. Lee, C. Y. Kang, J. S. Kim, S. J. Yoon, The selective detection of C_2H_5OH using SnO_2-ZnO thin film gas sensors, Sens. Actuators B 123 (2007) 318–324
[15] M. S. Wagh, L. A. Patil, T. Seth, D. P Amalnerkar, Surface cupricated SnO_2–ZnO thick films as a H_2S gas sensor, Mat. Chem. Phys. 84 (2004) 228-233.
[16] N. Yamazoe, Y. Kurokawa, T. Seiyama, Effect of additives on semiconductor gas sensors, Sens. Actuators 4 (1983) 283-289.
[17] B.C. Shin, M. Miyayama, H. Yanagida, Carbon monoxide gas sensitivity of CuO-infiltrated ZnO ceramics, J. Mat. Sci. Lett. 13 (1994) 719-722.
[18] K. W. J. Wong, M. R. Field, J. Z. Ou, K. Latham, M. J. S. Spencer, I. Yarovsky, K. Kalantar-zadeh, Interaction of hydrogen with ZnO nanopowders – evidence of hydroxyl group formation, Nanotechnology 23 (2012) 015705-015713.
[19] T. Hilber, Letonja P., Marr R., Polt P., Siebenhofer M., Formation of submicron zinc particles by electrodeposition, Part. Part. Syst. Charact. 19 (2002) 342-347.
[20] R. M. Rioux, H. Song, M. Grass, S. Habas, K. Niesz, J. D. Hoefelmeyer, P. Yang, G.A. Somorjai, Monodisperse platinum nanoparticles of well defied shape: synthesis, characterization, catalytic properties and future prospects, Topics in Catalysis, 39 (2006) 167–174.

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