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A Review Article on Zirconia based Thick Film Gas Sensors

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Abstract: ***Pollution has raised its ugly head high in the global environment. It created tremendous disasters of global warming. To face such disasters, is a very challenging for mankind. Many gases released by the vehicles and industries contribute the pollution and ultimately the global warming. Gases beyond certain limit can affect the living beings. So, there is a need to detect the gaseous pollutants in the environment, even at trace levels. Many researchers are working already to detect the hazardous gases in the environment and hence to develop the gas sensors at their best level. Researchers are well known about the hazards of different gases released by any means in the open environment. Still, the action has not been initiated in the desired proportion to save the environment from the pollution and its hazards. Also, the researchers have the responsibility to aware the society from the pollution hazards. The aim of the present study is, to well acquaint about the thick film ZrO_2 and their nanocomposite gas sensors. Gas sensors can be fabricated and developed the by utilizing the pure and surface activated ZrO_2 and their nanocomposites so that, they could be able to detect various gases at trace levels (ppm / ppb).***

Keywords: ***Nanostructured ZrO_2, Synthesis, Thick Films, Gas sensors, Characterizations, Polluting gases, etc.***

I. INTRODUCTION

There is a strong interest in the development of wide band gap semiconductor gas sensors for monitoring the gaseous species in the open environment, volatile and inflammable fuel leak in various fields, exhaust diagnosis and emissions from industries, etc. In 1950s, it was discovered that the electrical properties of some metal oxides get changed [1] when they are exposed to oxidizing or reducing gases. In 1962, Seiyama et al. [2] proposed the concept of gas monitoring using ZnO in the form of thin films. During the same year, Taguchi [3] put forth his concept that the SnO_2 also acts as a gas sensor. Figaro Engg. Inc. [4] made efforts in fabrication of gas sensors and has made available these sensors for commercial use, since 1968. Taguchi gas monitor was fabricated from partially sintered SnO_2 bulk device whose resistance in air is very high and falls down when exposed to reducing gases and combustible gases, viz. H_2, CH_4, VOCs, etc. To study and develop the fundamentals of the gas sensing mechanism, the semiconducting sensors are modified by simple mechanochemical addition, either salt of metals (viz. Bi, Sr, Al, In, Cu, Sn, Fe, Ru, Pt, Pd, etc.), or their oxides in the base materials which is referred to as doping. Metal oxides viz. SnO_2, ZrO_2, ZnO, Fe_2O_3, TiO_2, WO_3, etc. have also been used as gas sensors. The concentration of the gas in the environment which produces an undesirable and disastrous change in the physical, chemical or biological characteristics of air, soil and water that can harmfully affect the living beings is called as pollution. Heavy industrialization, uncontrolled urbanization and careless application of technology can cause pollution [5-10]. The main culprits behind all such hazards are the toxic, inflammable and explosive gases. Gases play the key role in many industrial or domestic activities. In the last twenty years, the demand for gas detection and monitoring has increased. Particularly, the awareness of the need to protect the environment has grown.

II. TYPES OF SENSORS

Table 1: Types of sensors and their particulars

SENSORS	Types of Sensors		Detection Capability
	PHYSICAL	Magnetic	Magnetic moment, magnetic flux density, etc.
		Mechanical	Strain, stress, torque, flow, displacement, force, pressure, acceleration, etc.
		Thermal	Flux, thermal conductivity, heat flow, specific heat, temperature, etc.
		Electrical	Conductivity, voltage, resistance, charge, current, inductance, etc.
		Optical	Refractive index, reflectivity, polarization, light intensity, wavelength, etc.
		Acoustic	Wave (amplitude, phase polarization), spectrum, wave velocity, etc.
	CHEMICAL	Biological	Concentration of gaseous species in additives, food freshness, disease diagnosis, etc.
		Humidity	Concentration of moisture content in environment or in industries.
		Gas	Concentration of gaseous species in the environment.

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III. GAS SENSORS AND THEIR APPLICATIONS

Gas sensor is a device which when exposed to the gaseous species, produces a proportional output signal corresponding to its odor, concentration, contents, etc. Gas sensor detects the odor and concentration of gases, below the detection limit of human sense organs.

The output signal produced by gas sensor may be in the form of electrical, mechanical or magnetic in nature. Gas sensors find applications in numerous fields, viz. fire detectors, gas leakage detectors, controllers of ventilation in cars and planes, alarm devices for hazardous gases in the work places, etc. The detection of volatile organic compounds (VOCs) or smells generated from food or household products has also become increasingly important in food industry, in indoor air quality and multisensory systems. These are popularly referred as electronic noses [11-15].

Following are the reported examples of applications of gas sensors and electronic noses.

A. Safety
1) Fire detection
2) Leak detection
3) Toxic/flammable/explosive gas detectors
4) Personal gas monitor

B. Environmental Control
1) Weather stations
2) Pollution monitoring

C. Automobiles
1) Car ventilation control
2) Filter control
3) Gasoline vapor detection
4) Alcohol breath tests

D. Food
1) Food quality control
2) Process control
3) Odor detection

E. Medicine
1) Breath analysis
2) Disease detection

Metal oxide based solid state gas sensors are the best selection to the development of commercial gas sensors for a wide range of applications.

The great interest of industrial and domestic solid state gas sensors comes from their versatile advantages like portable size, high sensitivity in detecting very low concentrations (ppm, ppb or sub ppb level) of a wide range of gaseous chemical compounds and low cost.

On the other hand, traditional analytical instruments are expensive, complicated and bulky. Solid-state chemical sensors have been widely used but they also suffer from limited measurement accuracy and problems of long-time stability. Recent advances in nanotechnology, as far as the synthesis of materials is concerned, produces novel classes of nanostructured materials with enhanced gas sensing performance.

This technology dramatically increases the performance of solid state gas sensors. Gas sensors are needed to; minimize the health hazards, avoid the hazards of global warming, avoid the cruelest episodes and detect and control the pollutants in the environment in the form of gas or moisture.

IV. PERFORMANCE MEASUREMENT OF SENSORS

The characteristics that are desirable to measure the sensing performance of any sensor are as follows [16-18].

A. Gas Response (S)

Gas response is defined as the ratio of the change in conductance of the sensor in presence and absence of target gas to the conductance in absence of target gas (air). The gas response (S) is given by the relation;

$$S = \frac{G_g - G_a}{G_a}$$

Where, G_g and G_a are the conductance of sensor in air and in a target gas medium, respectively. The percentage gas response is given by the relation;

$$\% S = \frac{G_g - G_a}{G_a} \times 100\%$$

B. Selectivity

Selectivity is defined as, the ability of a sensor to respond to certain gas in the presence of mixture of number of gases. Selectivity is also termed as, specificity. A good gas sensor should be very much selective for a particular gas in presence of some other gases or mixture of gases, even at high concentrations.

C. Selectivity Factor (K)

Selectivity factor of one gas over other is defined as, the ratio of the maximum response of the target gas to the maximum response of the other gas at optimum conditions, viz. temperature, gas concentration, etc.

$$K = \frac{S_{target\ gas}}{S_{gas}}$$

D. Response Time (RST)

The time taken for the sensor to attain ninety percent of the maximum increase in conductance on exposure of the target gas, is known as response time.

A. Recovery Time (RCT)

The time taken by the sensor to get back ninety percent of the maximum conductance when the flow of gas is switched off, is known as recovery time.

F. Sensitivity

The sensitivity of a sensor is defined as the change in output of the sensor per unit change in the parameter being measured.

G. Repeatability

The ability of the sensor to produce the stable response upon number of successive exposures of target gas is called as repeatability.

H. Long Term Stability

The ability of the sensor to produce the stable response over longer time span, irrespective of the number of target gas exposures is called as long term stability.

I. Detection Limit

It is the lowest concentration of the gas (ppm / ppb) that can be detected by the sensor under given conditions, particularly at a given temperature.

J. Resolution

The lowest value of difference of gas concentration (ppm / ppb), that can be distinguished by the sensor is called as resolution. It is measured in ppm.

K. Linearity

It is the relative deviation of an experimentally determined calibration graph from an ideal straight line.

L. Operating Temperature

It is usually the temperature that corresponds to maximum response to a particular gas.

V. LITERATURE SURVEY

K. M. Garadkar *et. al.* [19] successfully prepared room temperature H_2 gas sensor from nanostructured ZrO_2 material by employing thick film technique. The highest response was about 50 ppm for H_2 gas and for other gases it was poorer about 1000 ppm at room temperature. Quick response and fast recovery are the main features of this sensor. This technique is found not only the time saving but also an energy saving technique. Gas response decreases with increasing temperature from room temperature to 150^{o}C, which mean that it is not suitable to use at higher temperature than the room temperature. Efforts were taken to enhance the sensitivity of the sensor to H_2 and CO_2 gases at different operating conditions.

J. Aarik *et. al.* [20] recorded how growth rate of HfO_2 and ZrO_2 decreased with increasing flow rate and pressure of N_2 carrier gas. Thin films by Atomic Layer Deposition technique were obtained with higher density, higher refractive index and lower concentration of residual chlorine at higher carrier gas flow rate. Comparing effect of flow rate and increasing pressure of the carrier gas, it results in higher consumption of the carrier gas. High flow rates at low pressure rather than high pressure at low flow rate should be preferred for optimizing ALD (Atomic Layer Deposition) process.

M. T. Colomer *et. al.* [21] formed and studied thick films cermet of ZrO_2-Y_2O_3-TiO_2/Ni onto Yttrium Stabilized Zirconia (YSZ) substrate. The thick film cermet showed good adherence and chemical and mechanical compatibility with YSZ electrolyte. Sintering was carried out without introducing any reducing atmospheric temperature, which will allow co-sintering of all the components in one unique stage. At over potential value higher than 730 mV, the Ni oxidation takes place. Above this, a passivation effect was observed.

S. Bertaux *et. al.* [22] obtained thin nanocrystallite Ta_2O_5 and ZrO_2 films deposited onto SiO2 flakes using a liquid route synthesis. The study was carried out to sintering of nanocrystalline Ta_2O_5 and ZrO_2 films compared to that of TiO_2 films. It was found that, effect of substrate is noticeable on crystallization process but not on grain growth. Though it is not affect the crystallization, but substrate retards the phase transformation for the zirconia films as it is previously observed for TiO_2 films.

Kuyyadi P. Biju *et. al.* [23] prepared sol-gel derived TiO_2:ZrO_2 multilayer thin films for humidity sensing application. These films showed less drift and less/low hysteresis compared to pure TiO_2. The response and recovery time of TiO_2/ZrO_2 thin films were recorded at 54 s and 126 s respectively.

W. Cao *et. al.* [24] carried out their study on mechanical alloying and thermal decomposition of $(ZrO_2)_{0.8}$-$(\alpha\text{-}Fe_2O_3)_{0.2}$ powder for gas sensing applications. In this study, the material thermal decomposition property correlates with the behaviour of direct conductivity and gas sensing property. The $(ZrO_2)_{0.8}$-$(\alpha\text{-}Fe_2O_3)_{0.2}$ material is used to sense O_2 gas. Some drawbacks are also recorded, viz. 1) time required to carry out the experiment is up to 120 h., 2) high energy ball milling machine is required to prepare the material, 3) in first 2 hours milling, the average size of particle is reduced from 100 nm to 25 nm and for the further time up to 120 hours, particle size reduced to 8 nm from 25 nm. That is lot of time is required for this process, 4) beyond 650^{o}C, the oxygen vacancy concentration decreases hence, its usefulness of conductivity and gas sensitivity are also reduced.

Ken-ichi Shimizu, *et. al.* [25] has successfully obtained impedance metric gas sensor based on Pt and WO_3 co-loaded TiO_2 and ZrO_2. This sensor is useful as NO_x gas sensing equipment. It gives very quick response. A linear correlation between the response magnitude and to the logarithm of NO_2 and NO concentration from 10 to 570 ppm. Nearly equal response for both NO and NO_2 is recorded. The temperature requirement for testing is about 500^{o}C; i.e. to check the performance of sensor, a furnace operating between 200^{o}C-500^{o}C is required.

M. Cassir *et. al.* [26] carried out the synthesis of ZrO_2 thin films by atomic layer deposition. They studied Growth kinetics, structural and electrical properties of ZrO_2 thin films. Zirconia deposit study by ALD determines the dependency of growth rate versus temperature. Impedance spectroscopy confirmed the electrical properties of ZrO_2 and the very low porosity of the deposited layer. Operating temperature used for the experimentation was in the range from 280^{o}C to 400^{o}C.

H. Bensouyad *et. al.* [27] successfully studied structural, thermal and optical properties of TiO_2:ZrO_2 thin films. The thin films of TiO_2:ZrO_2 were prepared by sol-gel method. The test sample of 5% ZrO_2 doped TiO_2 was used. It was observed that, the film is transparent in visible range and opaque in UV range. They recorded that, the grain sizes may increase due to phase transition and increased density of layers. It also resulted in the decreased porosity of the film. Requirement of operating temperature for the study is about 350^{o}C.

N. Izu *et. al.* [28] investigated the sensing properties of resistive oxygen sensors using zirconia doped ceria in a model gas of the exhaust gas prepared by propane combustion gas. The CeO_2-ZrO_2 paste was screen printed on the Pt electrode side of the Al_2O_3

substrate. So, the thick films of the material were formed. Resistance of the thick films was measured as a function of excess oxygen factor, λ. The sensor using these thick films could be used as a λ sensor, which can detect whether the exhaust gas is reach or lean in the temperature range from 723 to1073^{o}K.

William C. Maskell [29] studied the progress in the development of zirconia gas sensors to check O_2 gas. An oscillatory mode of pump gauge sensor is described with tolerance to leakage due to deterioration of the seal. In this method, planer thick film sensors were prepared and tested which operate effectively in the atmospheric conditions. The sensor was made on the alumina substrate by printing first Pt electrode which was then overprinted with ZrO_2 electrolyte followed by second electrode. The main feature includes the reducing unit cost of the sensor for O_2 gas detection. Also, sensors were made showed characteristics typical of atmospheric devices. However, this technique is unable to sense the other gases than oxygen gas and the operating temperature requirement is somewhat high.

Wenqing Cao *et. al.* [30] successfully investigated ZrO2 based α-Fe_2O_3 thick film gas sensor for low operating temperature. Amorphous like solutions of powders of xα-Fe_2O_3-(1-x)ZrO_2 powder were derived using high energy ball milling technique and their physical and microstructural properties were studied. The powder samples were formed into paste and screen printed onto ceramic substrates with Au electrodes to obtain the O_2 gas sensors. Very good O_2 sensing properties were obtained at a low operating temperature of 320^{o}C.

Noria Izu *et. al.* [31] investigated a temperature compensating material for a resistive oxygen sensor using Ceria-Zirconia sensor material and Ceria-Yttria temperature compensating material for Lean-Burn engine. Ceria-Yttria and Ceria-Zirconia powders were prepared and then pastes were obtained by mixing the fine Yttria doped Ceria or Zirconia doped Ceria powder. The paste was screen printed on Al_2O_3 substrates. The film thickness was in the range from 6-8 µm. Pt material was used as the electrode material. The output of the sensor was approximately independent of the temperature in a wide range from 773 to 1073^{o}K and detection limits were clarified.

Arnold O. Isenberg [32] is the United States patented work on solid state filter for gas sensors. A solid state filter in combination with a gas sensor to protect the gas sensor from deterioration and contamination by particulate and certain gaseous matter especially O_2 gas present in the gas environment being monitored. The industrial gas environment sensed with respect to oxygen by eliminating other gaseous and particulate matter is an important invention of the work.

Boris Farber [33] is the United States patented work on method for improving performance and longevity of solid electrolyte gas sensor. In this work, he provided a method for activating a zirconia O_2 sensor which detects the oxygen concentration of the surrounding atmosphere by means of a zirconia element that has a porous electrode formed on both sides of an oxygen ion conductor. Other than O_2, the other gases are not detected by this method.

Kurachi *et. al.* [34] successfully fabricated a gas sensor for detecting the concentration of a gas such as oxygen, nitrogen oxide, sulphur oxide, carbon monoxide or carbon dioxide contained in exhaust gas from an internal combustion engine. This prevents emission of incompletely burnt gas, allows exhaust gas to be purified there by reducing the fuel consumption. This sensor is stable against high temperature exhaust gas. Such type of gas sensor is generally operated in predetermined high temperature region by using a heater provided with it. The main drawback is that it has somewhat more complex structure. Also the separation may occur inside the gas sensor during its use. This is US patented work.

Da Yu Wang *et. al.* [35] successfully fabricated ammonia gas sensor. This US patented invention leads to manufacture of sensor which sense the ammonia gas. It also senses the NO_x gas. This sensor includes a reference electrode, ammonia sensing electrode and an electrolyte disposed in between. The main material selected for electrode is from the group consisting of oxides of vanadium, tungsten, molybdenum, and combinations comprising of at least one of the foregoing main materials, and an electrically conductive metals, electrically conductive metal oxides and combinations comprising of at least one of the foregoing. This sensor shows high response to NH_3 gas about 1.5 ppm and to NO about 15 ppm. It is used to develop regeneration cycle of NO_x traps. An important feature of this sensor is that it has high sensitivity and selectivity. It is only used to sense NH_3 gas as other gas response of the sensor is much less. If it is used to detect only ammonia, then it also shows response to NO_x gases up to 15 ppm.

Robert M. Sinkevitch [36] fabricated solid electrolyte exhaust gas oxygen responsive sensor with Pt exhaust gas electrode and porous ceramic coating of rhodium on the electrode. Due to porous rhodium coating, this sensor is also responsive to NO_x. rhodium permits a gamma alumina porous overcoat on a sputtered platinum film serving as exhaust gas electrode on zirconia solid electrolyte. With this sensor, nitrogen oxide response is obtained without losing oxygen responsiveness. The assembling of the sensor is complex. It is only used to detect NO_x and no other gases.

Roswell J. Ruka *et. al.* [37] successfully developed oxygen sensor for monitoring gas mixtures containing hydrocarbons. For their invention, they got US patent in 1996. A solid electrolyte chemical cell used for sensing purpose. An electrochemical cell includes a solid electrolyte that is preferably made of nonporous stabilized zirconia, ZrO_2 doped with yttria preferably Y_2O_3. Main object of this sensor is to monitor gas concentrations of gas mixtures containing gaseous hydrocarbons and gaseous H_2O and /or CO_2. The main feature of the sensor is, signal noise is effectively reduced by maintaining a constant temperature in the area of the electrochemical cell and providing a monitored gas at chemical equilibrium when contacting the electrochemical cell. The drawback of this sensor is its bulky instrumentation in comparison with other gas sensors.

Hiroyuki Shindo *et. al.* [38] devised a method for manufacturing sensor element for gas sensor. This invention got US patent in 2011. This is study type invention in which ZrO_2 gas sensor element manufacturing is studied and gives the remedial measures. They also found the reason of instability of an oxidation-reduction in various electrodes. The object of this invention is to provide a method for manufacturing a sensor element capable of improving the yield of the product and realizing a gas sensor having high reliability.

Tao liu *et. al.* [39] successfully prepared an electrochemical sulfur sensor based on ZrO_2 (MgO) as solid electrolyte and ZrS_2 + MgS as an auxiliary electrode. The sensor measures the sulfur content. ZrS_2 + MgS was synthesized on the surface of commercial ZrO_2 electrolyte at1573^oK for 8 h. The synthesized material is assembled with the help of quartz tube. The auxiliary electrode achieves good densification and adheres to the substrate firmly. In this study, readings are not get directly by instrument but an empirical formula based on relationship between sensor e.m.f. and sulfur content is used to calculate the sulfur content.

Jiahe Liang *et. al.* [40] by doing chemical treatment on a thin film of pure ZrO_2 nano-powders, characterization and synthesis was carried out via sonochemical method. It was found that the environmental toxicity from this material is zero. The material causes eye irritation, irritation of the mucus membranes and respiratory tract. The material is not expected to bio-degrade.

D. G. Lamas *et. al.* [41] studied the crystal structure of pure ZrO_2 nano-powders. The crystal structure of undoped zirconia nano-powders synthesized by different wet chemical routes has been investigated by synchrotron X-ray diffraction. The outcome of this work is that, the pure zirconia nano-powders with average crystallite sizes ranging from 5 to 10 nm exhibit the tetragonal phase.

M. M. Rashad *et. al.* [42] studied the effect of thermal treatment on the crystal structure and morphology of zirconia nano-powders produced by three different routes. The three processing routes, namely, conventional precipitation (CP), citrate gel combustion(CGC), and micro-emulsion refined precipitation (MRP). The characterizations were carried out by XRD, SEM, FT-IR spectroscopy and UV-visible absorption spectrum. The result showed that the CP route lead to the formation of tetragonal ZrO_2 phase with low crystallinity at 700^oC. this phase was transformed to monoclinic ZrO_2 phase at temperatures ranging from 1000 to 1200^oC. CGC route led to the formation of monoclinic phase in the temperature ranges from 1000 to 1200^oC. MRP technique formed tetragonal phase with high crystallinity compared to other routes at 700^oC and produced tetragonal phase was inverted to cubic phase by increasing the calcination temperatures from 1000 to 1200^oC.

Pinggen Rao *et. al.* [43] studied the effect of Al_2O_3 addition on ZrO_2 phase composition in the Al_2O_3-ZrO_2 system. Al_2O_3-ZrO_2 powders with 15, 50 and 85 wt % Al_2O_3 were prepared by mixing very pure α-alumina powder with $Zr(OH)_4$ gel synthesized by the precipitation method. This mixture was calcined for 2 h at 400 to 1300^oC. Phase composition was characterized by thermal analysis, X-ray diffraction and TEM.

J. M. Dominguez *et. al.* [44] studied the surface and catalytic properties of Al_2O_3-ZrO_2 solid solutions prepared by sol-gel method. A series of Al_2O_3-ZrO_2 solid solutions were prepared by co-hydrolysis. A systematic study was performed by X-ray diffraction.

S. N. B. Hodgson *et. al.* [45] studied the role of Al_2O_3 impurities on the microstructure and properties of Y-TZP. A study has been carried out into the effects of variously dispersed Al_2O_3 at the 0-1 wt % level on the sintering characteristics, microstructure, phase composition and mechanical properties of Yttrium stabilized tetragonal zirconia poly-crystal (Y-TZP). The result showed, these levels of Al_2O_3 can enhance sintering at low temperatures, but also cause an exaggerated grain growth and reduction in sintered density for higher sintering temperatures, with corresponding changes in the mechanical properties.

G. B. Shelke *et. al.* [46] studied the surface activated nanostructured zirconia thick films for the detection of ppm level oxygen gas operable at room temperature. Nanostructured ZrO_2 powder was synthesized by disc type ultrasonicated microwave assisted centrifuge technique. Thick films of nanostructured unmodified ZrO_2 powder were fabricated by screen printing technique. These films were surface functionalized (activated) by SrO_2 for different intervals of time. The characterizations, viz. surface morphology, chemical composition and crystal structure of the pure and modified nanostructured Zirconia powder by Strontium Oxide were investigated. Electrical characterizations, viz. I-V characteristics and conductivity profile also studied. Nanostructured pure and

surface activated ZrO_2 by SrO_2 tested for gas sensing performance for the gases, viz. H_2, CO_2, O_2, NH_3, C_2H_5OH, LPG, Cl_2 and H_2S. The selected material gives significant response and it is highly selective to O_2 gas among all other gases.

G. B. Shelke *et. al.* [47] carried out the work on synthesis, characterizations and gas sensing performance of $Zr_{(0.50)}Sn_{(0.50)}O_4$ nanocomposite material. The material was prepared by using synthesized ZrO_2 and SnO_2 powders by taking their 1:1 proportion. Thick films of nanostructured pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ powder were fabricated by screen printing technique. These films were surface functionalized by SrO_2. The surface morphology, chemical composition, crystal structure has been investigated by FESEM, EDAX, XRD, etc. Electrical and H_2S gas sensing performance of the thick films were also studied along with other parameters, viz. Response, recovery time and the long term stable nature.

G. B. Shelke *et. al.* [48] studied the surface functionalized $Zr_{(0.75)}Sn_{(0.25)}O_4$ by SrO_2 thick films as H_2S gas sensors. Pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick film was almost less sensitive to H_2S. Among various additives tested, SrO_2 in $Zr_{(0.75)}Sn_{(0.25)}O_4$ is outstanding in promoting the H_2S sensing. Surface modification by activation is one of the most suitable methods of modifying the surface of thick films. The sensor has good selectivity to 5 ppm H_2S gas against LPG, NH_3, O_2, CO_2, Cl_2, H_2 and C_2H_5OH at room temperature.

VI. MATERIAL SYNTHESIS AND THICK FILM FABRICATION

Fig. 1 (a): Disc type ultrasonicator Fig. 1 (b): Microwave treatment followed centrifuge technique

Fig. 1 (a) shows disc type ultrasonicator and Fig. 1 (b) shows microwave treatment followed centrifuge technique. Nanostructured ZrO_2 powder was synthesized by disc type ultrasonicated microwave treatment followed centrifuge technique [49], by hydrolysis of AR grade zirconium oxychloride in aqueous-alcohol solution. An initial aqueous-alcohol solution was prepared from distilled water and propylene glycol in the ratio of 1:1. This solution was then mixed with 1M aqueous solution of zirconium oxychloride in the ratio 1:1. The special arrangement was made to add drop wise aqueous ammonia (0.1 ml / min.) with constant stirring until the optimum pH of solution becomes 7.9. After complete precipitation and centrifugation, the hydroxide was washed with distilled water until chloride ions were not detected by $AgNO_3$ solution. Then the precipitate was allowed for ultrasonication and then kept in a microwave oven for 10 minutes with continuous on-off cycles, periodically, followed by calcination at 500^{o}C for 2 hrs in muffle furnace. The dried precipitate was ground by agate pestle-mortar to ensure sufficiently fine particle size and re-calcined in a muffle furnace at 500°C for 2 hrs, to eliminate the organic impurities, if present. Thus, the dry white powder of nanostructured ZrO_2 has been prepared to use.

VII. THICK FILM FABRICATION TECHNIQUE

The use of thick film technology in the production of chemical sensors has opened up the possibility of manufacturing sensors in a cost effective manner. Such properties of a thick film sensor are highly desirable for chemical applications. Furthermore, thick film technology has the ability to produce the sensors from nano-scaled materials. This is an advantage because minute sample volume is required. Also, the portability of the interface instrument for the sensor can be realized.

Thick film technology based on glass and ceramic compositions is very stable in severe conditions such as high temperature or corrosive environments. Deposition of the layers is most commonly carried out by using screen printing for high volume and low cost production. Each layer is printed with a paste comprising of a functional material and a temporary organic vehicle. After deposition, solvent was removed by drying followed by firing, in order to eliminate the organic binder and sinter the materials. Glass frits are commonly used alone for over glazes and as a permanent binder in thick film technology [50-52]. Commonly ceramic substrates made of mostly alumina (Al_2O_3), silicon, glass-ceramic and sapphire with appropriate surface finish are used.

The change in resistance for thicker films is large as compared to thinner ones [53]. A wide range of miniature sensors have been developed in recent years based on thin and thick film technology [54] and using surface mounting devices (SMD), complex circuits are realized in hybrid form [55]. The thick and thin film technologies are extensively used in the area of microwaves [56] to realize the components for microwave integrated circuits like strip lines. In integrated optics [57], thick and thin film technologies are used to realize optoelectronic components like photo-conducting CdSe cells. The surface acoustic wave (SAW) devices are also based on thin film technology [58]. Thick film technology involves screen printing methodology and thick film fabrication.

A. Screen Printing Technique

Screen-printing is a simple method that allows the production of low cost and robust oxide thick film sensors with good reproducibility, provided that, the starting materials are well controlled [59]. It involves printing the thixotropic paste through a mesh screen which defines the desired pattern on the substrate. The thixotropic paste of the semiconducting material contains of finely divided particles of basic sensor material and additives along with organic binders, whereas, the substrate is usually made up of ceramic, steel, glass, etc. The sensor material has a relatively high viscosity but when forced through the screen mesh by the squeegee blade, the paste undergoes sheer thinning which allows it to penetrate through the screen mesh which defines the desired pattern on the substrate. Upon contact with the substrate, the sensor material returns to its viscous state forming the desired pattern. Pattern thus formed using screen printing technology have thickness which ranges from 30 to 40 µm and is thicker than those obtained by other printing techniques. Thus, printing such films using screen printing is called as, 'Thick Film Technology'.

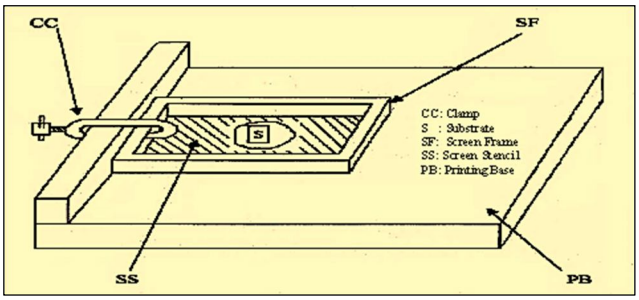

Fig. 2: Screen printing set-up board

As shown in Fig. 2, the screen printing set-up contains screen base, frame, stencil, squeegee and substrate. The screen stencil is made up of a fine mesh of polyester, nylon material which is stretched and mounted on preferably a wooden frame. The photosensitive emulsion is spread over the mesh and with the help of photographic method the desired patterned is obtained. The squeegee is a flexible polyurethane blade (sometimes neoprene) held in a rigid mount or handle. It is used to spread the thixotropic paste evenly over the screen so that the paste oozes down through the pores (open areas) of the screen mesh onto the substrate. The detailed procedure was adopted in making stencil, cleaning the substrates and screen printing [60].

B. Stencil Preparation

1) A four times larger piece of chromline film (than the required pattern to be developed) was taken.
2) This piece was pasted with a solution comprising of thick film coating lotion and sensitizer mixed in the ratio 20:1.
3) The chromline film was allowed to dry and remove the protective layer on the top of chromline film.
4) The mask was placed with required pattern in contact with chromline film and exposed it to solar radiations for appropriate time interval (~ 2 min.).
5) The screen was washed in water bath, the portion which was not exposed to light dissolved in water.
6) The windows for sensor patterns are ready to print.

C. Cleaning of Substrates

1) The substrates were kept in chromic acid for 15 min.
2) The substrates were washed thoroughly in water to remove the acid.
3) The washed substrates were immersed in a soap solution for 5 min.
4) Substrates were finally cleaned in ultrasonic cleaner and dried under an IR lamp for 30 min.

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D. Screen Printing Mechanism

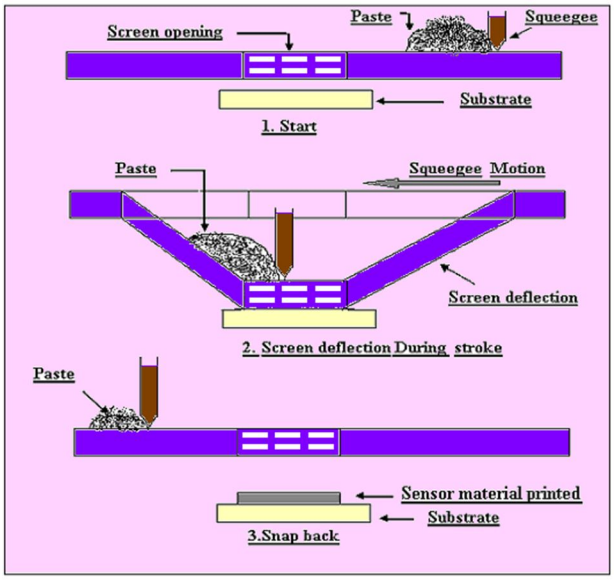

Fig. 3: Screen printing mechanism

The screen is held at about few millimeters above the substrate on a printing set up board (Fig. 3). The required thixotropic paste is kept on the top surface of stencil and squeegee pushes the paste and poured through the pores while it moves from one end to the other. The sensor patterns of desired shape are printed on the glass substrates.

These samples are then subjected to a temperature in the range of 70-130^{o}C for drying under an IR lamp. Curing is done in order to avoid the blistering of the film. It has two steps: removal of organic binder and high temperature curing / firing. In the first step, the residues of organic binder (even after drying process) are eliminated by heating at low temperature. In the second step, the film is subjected to a furnace under controlled conditions. The chemical reactions that take place, give the required electrical and physical properties of the film.

VIII. STATIC GAS SENSING SYSTEM

Fig. 4 shows the block diagram of the static gas sensing system. The sensor element, heating unit, dc power supply, gas inject unit, temperature measuring unit, current meter (pico-ammeter), glass dome and steel base plate are the major components of static gas sensing system. Heating unit is fixed on the base plate. It provides the desired temperature to sensor for its proper performance. Sensor sample to be tested was mounted above the heater. Cr-Al thermocouple is mounted to measure the temperature. The output of thermocouple is connected to temperature indicator. Inlet gas port was fitted at one of the ports of base plate. Gas concentration inside the static system is achieved by injecting a known volume of test gas by gas inject syringe. 0-30 V d. c. is applied to the sensor element constantly for measurement of I-V characteristics and 30 V d. c. for gas sensing and the current is measured by pico-ammeter [60].

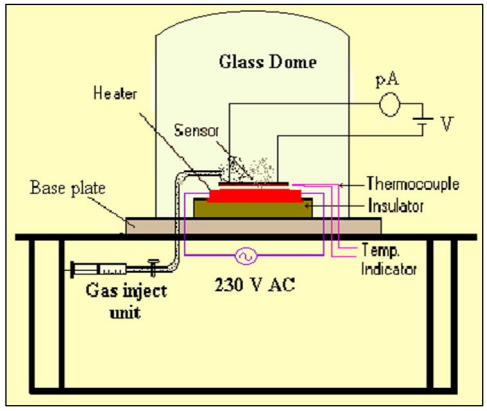

Fig. 4: Block diagram of static gas sensing system

IX. CONCLUSIONS

A review of the existing literature suggests that the modified and unmodified ZrO_2 thick films possess in several important areas of application of modern microelectronic techniques, because of their uses in production of advanced infrared detectors and sensors for sensing toxic gases. The parameters, on which the performance of the gas sensor depends, can be optimized for better performance of the sensor. Operating temperature, additive concentration (doping concentration in wt % and dipping time), calcination temperature, etc. are the parameters of the sensor to be optimized. The review also reveals that, very few researchers studied on ZrO_2 thick films. Also, very few attempts have been made to study the dipping time variation with the response of gas. Hence, it is the need to study the effect on structural, electrical and gas sensing properties by changing dipping time. There is a great space to work for the development of ZrO_2 based gas sensors.

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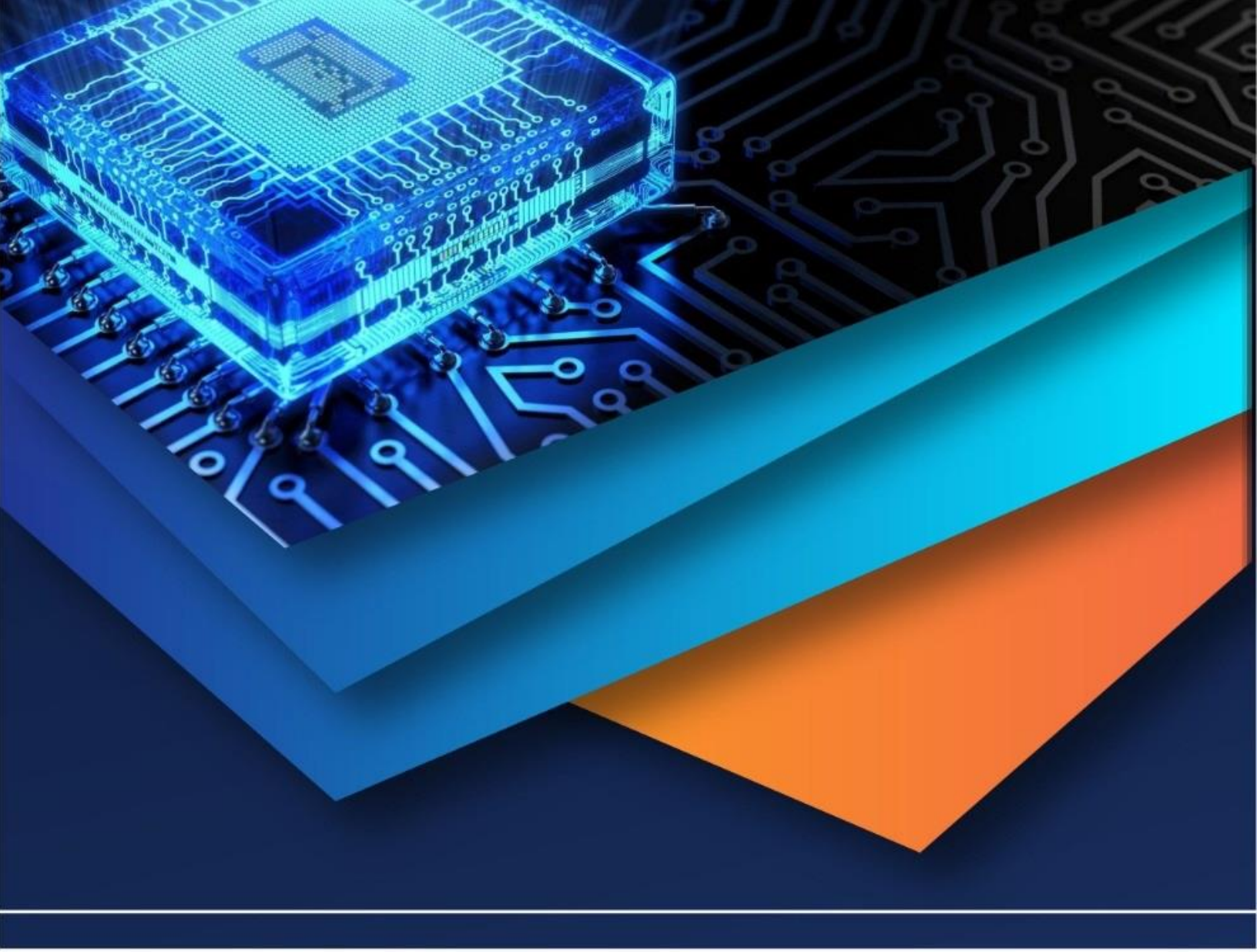
REFERENCES

[1] Wagner C., J. Chem. Phys. 18 (1950) pp. 69.
[2] Seiyama T., Kato A., Fujiishi K., Nagatanui M., Anal. Chem. 34 (1962) pp. 1502.
[3] N. Taguchi, A metal oxide gas sensor, Japanese patent No. 45-38200 (1962).
[4] http://www.figarosensor.com, available online.
[5] Dasmann R. F., Environmental conservation, 4th Ed., John Wiley and Sons, Inc., New York (1976) pp. 310-338.
[6] Moore P. D., Pollution: Too much of a good thing, Nature (London) 374 (1995) pp. 117-118.
[7] Brooks M., Coghlan A., Live and let live, New Scientists (1998) pp. 46-49.
[8] Durham W. B., Industrial Pollution, Sax, N. I., Van Nostrand Reinhold Co., NYK (1974) pp. 10-35.
[9] Eckerman I., Bhopal Gas Catastrophe 1984: Causes and Consequences, Encyclopedia of Environmental Health (2011) pp. 302-316.
[10] Heylin M., Bhopal: Ten years after, Chem. and Eng. News 72 (51) (1994) pp. 18-32.
[11] Barsan N., Koziej D., Weimar U., Metal Oxide-Based Gas Sensor Research: How to? Sens. Actuators B 121 (2007) pp. 8-35.
[12] Colin Finn, Sorcha Schnittger, Yellowlees, Lesley J., Love Jason B. "Molecular approaches to the electrochemical reduction of carbon dioxide", Chem. Communications 10 (2012) pp. 1392-1399.
[13] Monastersky, A burden beyond bearing, Nature 458 (2009) pp. 1091–1094.
[14] Air Pollutant Emission Factors, Final Report, Resources Research, Inc., Reston, VA, Durham, NC (1970) Contract No. CPA-22-69-119.
[15] Ceresana, "Market Study Ammonia" (2012).
[16] Kirschbaum B., Sica D., Anderson F. P., Urine electrolytes and the urine anion and osmolar gaps, J. Laboratory and Clinical Medicine 133 (6) (1999) pp. 597–604.
[17] Graham Solomans T. W., Fryhle C. B., Org. Chem., 8th Ed., (2004) pp. 497-498.
[18] Syed Kamrul Islam, Mohammad Rafiqul Haider, Sensors and Low Power Signal Processing, Springer (2010) ISBN No. 978-0-387-79391-7.
[19] Garadkar K. M., Shirke B. S., Patil Y. B., Patil D. R., Nanostructured ZrO_2 thick film resistors as H_2 gas sensors operable at room temperature, Sens. Transducers 11 (2009) pp. 17-25.
[20] Aarik J., Aidla A., Kasikov A., Mandar H., Rammula R., Sammelselg V., Influence of carrier gas pressure and flow rate on atomic layer deposition of HfO_2 and ZrO_2 thin films, Applied Surface Science 252 (2006) pp. 5723-5734.
[21] Colomer M. T., Jurado J. R., Thick film cermet of ZrO_2-Y_2O_3-TiO_2/Ni: Anodic polarization study, J. European Ceramic Society 19 (1999) pp. 143-148.
[22] Stephane Bertaux, Peter Reynders, Jean-Marc Heintz, Sintering of Nanocrystalline Ta_2O_5 and ZrO_2 films compared to that of TiO_2 films, J. European Ceramic Society 26 (2006) pp. 923-932.
[23] Biju Kuyyadi P., Jain Mahaveer K., Sol-gel derived TiO_2 : ZrO_2 multilayer thin films for humidity sensing application, Sens. Actuators B 128 (2008) pp. 407-413.
[24] Cao W., Tan O. K., Zhu W., Jiang B., Mechanical alloying and thermal decomposition of $(ZrO_2)_{0.8}$-$(\alpha$-$Fe_2O_3)_{0.2}$ powder for gas sensing applications, J. Solid State Chemistry 155 (2000) pp. 320-325.
[25] Shimizu Ken-ichi, Kashiwagi Kohichi, Nishiyama Hiroyuki, Kakimoto Shiro, Sugaya Satoshi, Yokoi Hitoshi, Satsuma Atsushi, Impedance metric gas sensor based on Pt and WO_3 co-loaded TiO_2 and ZrO_2 as total NOx sensing materials, Sens. Actuators B 130 (2008) pp. 707-712.
[26] Michel Cassir, Fabrice Goubin, Cecile Barney, Philippe Vernoux, Daniel Lincot, Synthesis of ZrO_2 thin films by atomic layer deposition: Growth kinetics, structural and electrical properties, Applied Surface Science 193 (2002) pp. 120-128.
[27] Bensouyad H., Sedrati H., Dehdouh H., Brahimi M., Abbas F., Akkari H., Bensaha R., Structural, thermal and optical characterization of TiO_2 : ZrO_2 thin films prepared by sol-gel method, Thin Solid Films 519 (2010) pp. 96-100.
[28] Noria Izu, Noriko Oh-hori, Woosuk Shin, Ichiro Matsubara, Norimitsu Murayama, Masaki Itou, Response properties of resistive O_2 sensors using $Ce_{1-x}Zr_xO_2$ thick films in propane combustion gas, Sens. Actuators B 130 (2008) pp. 105-109.
[29] William C. Maskell, Progress in the development of zirconia gas sensors, Solid State Ionics 134 (2000) pp. 43-50.

[30] Wenqing Cao, Ooi Kiang Tan, Weiguang Zhu, Jisheng S. Pan and Jiang Bin, Study of $x\alpha$ - Fe_2O_3 - (1 - x)ZrO_2 solid solution for low temperature resistive O_2 gas sensors, Sensors IEEE 4 (2003) pp. 421-434.
[31] Noria Izu, Sayaka Nishizaki, Woosuck Shin, Toshino Itoh, Maiko Nishibori, Ichiro Matsubara, Resistive O_2 sensor using Ceria-Zirconia sensor material and Ceria-Yitria temperature compensating material for Lean-Burn engine, Sensors 9 (2009) pp. 8884-8895.
[32] Arnold O. Isenberg, Solid state filters for gas sensors, (1979) United States Patent (US 4,151,060).
[33] Boris Farber, Method for improving performance and longevity of solid electrolyte gas sensor (2012) United States Patent (US 8,110,080 B1).
[34] Hiroshi Kurachi, Sang Jae Lee, Gas sensor (2009) United States Patent (US 7,497,933 B2).
[35] Da Yu Wang, Walter T. Symons, Robert J. Farhat, Carlos A. Valdes, Elizabeth M. Briggs, Kalus K. Polikarpus, Joachim Kupe, Ammonia gas sensors (2010) United States Patent (US 7, 828, 955 B2).
[36] Robert M. Sinkevitch, Solid electrolyte exhaust gas sensor with increased NOx sensitivity (1980) United States Patent (US 4,199,425).
[37] Roswell J. Ruka, Richard A. Basel, Oxygen sensor for monitoring gas mixtures containing hydrocarbons (1996) United States Patent (US 5,498,487).
[38] Hiroyuki Shindo, Kiyotaka Sugiura, Method for manufacturing sensor element for gas sensor (2011) United States Patent, (US 2011/ 0138875 A1).
[39] Tao liu, Lin Li, Jingkun Yu, An electrochemical sulfur sensor based on ZrO_2 (MgO) as solid electrolyte and ZrS_2+MgS as auxillary electrode, Sens. Actuators B 139 (2009) pp. 501-504.
[40] Jiahe Liang, Xin jiang, Ge Liu, Zhaoxiang Deng, Jing Zuang, Full Li, Yadong Li, Characterization and synthesis of pure ZrO_2 nanopowders via sonochemical method, Mater. Research Bulletin 38 (2003) pp. 161-168.
[41] Lamas D. G., Roso A. M., Anzorena M. S., Bellino M. G., Cebezas M. D., Walsoe de Raca N. E., Craievich A. F., Crystal structure of pure ZrO_2 nanopowders, Scripta Materialia 55 (6) (2006) pp. 553-556.
[42] Rashad M. M., Baioumy H. M., Effect of thermal treatment on the crystal structure and morphology of zirconia nanopowders produced by three different routes, J. Mater. Processing Technology 195 (1-3) (2008) pp. 178-185.
[43] Pinggen Rao, Mikio Iwasa, Jianqing Wu, Jiadong Ye, Yingjun Wang, Effect of Al_2O_3 addition on ZrO_2 phase composition in the Al_2O_3-ZrO_2 system, Ceramics Int. 30 (6) (2004) pp. 923-926.
[44] Dominguez J. M., Hernandez J. L., Sandoval G., Surface and catalytic properties of Al_2O_3-ZrO_2 solid solutions prepared by sol-gel methods, Applied Catalysis A: General 197 (1) (2000) pp. 119-130.
[45] Hodgson S. N. B., Cawley J., Clubley M., The role of Al_2O_3 impurities on the microstructure and properties of Y-TZP, J. Mater. Processing Tech. 92-93 (1999) pp. 85-90.
[46] G. B. Shelke, D. R. Patil, Surface activated nanostructured zirconia thick films for the detection of ppm level oxygen gas operable at room temperature, J. of Emerging Technology and Innovative Research, 7(4) (2020) pp. 58-65.
[47] G. B. Shelke, D. R. Patil, Synthesis, characterizations and gas sensing performance of SrO_2 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ nanocomposite thick films, Int. J. of Multidisciplinary Educational Research, 9 3(7) (2020), pp. 39-49.
[48] G. B. Shelke, D. R. Patil, Surface functionalized $Zr_{(0.75)}Sn_{(0.25)}O_4$ by SrO_2 thick films as H_2S gas sensors, 2nd Int. Conf. on Condensed Matter and App. Phy., AIP Conf. Proc. 1953, (ICC 2017) pp. 030270-1–030270-4.
[49] David Scanlon O., Graeme Watson W., Payne D. J., Atkinson G. R., Egdell R. G., Law D. S. L., Theoretical and Experimental Study of the Electronic Structures of MoO_3 and MoO_2, J. Phys. Chem. C 114 (2010) pp. 4636-4645.
[50] Ivanova T., Szekeres A., Gartner M., Gogova D., Gesheva K.A., Spectroscopic characterization of CVD molybdenum oxide films, J. Electrochem. Acta. 46 (2001) pp. 2215– 2219.
[51] Tomas S. A., Arvizu M. A., Zelaya-Angel O., Rodriguez P., Effect of ZnSe doping on the photochromic and thermochromic properties of MoO_3 thin films, J. Thin Solid Films 518 (2009) pp. 1332-1336.
[52] Jacq C., Maeder Th., Ryser P., Sensors and packages based on LTCC and thick-film technology for severe conditions, Sadhana 34 (2009) pp. 677-687.
[53] Ibrahim A., Al-Homoudi, Thakur J. S., Naik R., Auner G. W., Newaz G., Anatase, TiO_2 films based CO gas sensor: Film thickness, substrate and temperature effects, Appl. Surface Sci. 253 (2007) pp. 8607-8614.
[54] Kirby P. L., Pagan I. D., The Origins of Surface Mounting, Microelectronics Int. 4 (3) (1987) pp. 5-7.
[55] Mosca E., Gardella R., Simonin E., Varani E., Surface mounting applications a Comparison between technology, Proc. 5th European Hybrid Microelectronics Conference (1985) pp. 224.
[56] Ferraris G. P., Tessalvi A., Fine line photo-processing of thick film resistors for precision microwave hybrid thin film circuits, Proc. 5th European Hybrid Microelectronics Conference (1985) pp. 22.
[57] David J. Pena, et el., Template Growth of Photoconductive Metal−CdSe−Metal Nanowires, J. Phys. Chem. B 106 (30) (2002) pp. 7458-7462.
[58] Satyam M., Overview of hybrid microelectronics, Short term course on thick and thin films hybrid microelectronics, I. I. Sc., Bangalore (1986) pp. 1-3.
[59] Ram Kumar K., Thick Film Deposition and Processing Short Term Course on Thin and Thick Film Hybrid Microelectronics, Bangalore (1986) pp. 12.11-12.13.
[60] D. R. Patil, Studies on ZnO based gas sensors, Ph. D. Thesis, North Maharashtra University, Jalgaon, Ch. 2 (2007) pp. 56-72.



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