JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

"Gas sensors behaviours and properties"

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Abstract:

This is reviews of gas sensors which applicable and used in electronic systems for detection of toxic and harmful gases to date. Among the environmentally hazardous gases, namely; NO_2, NO, N_2O, H_2S, CO, NH_3, CH_4, SO_2, and CO_2. NO_2 is the most dangerous gas in terms of Threshold Limit Value (TLV) of 3 ppm. Therefore, the appropriate gas sensors have been investigated to measure the low concentration limit of each hazardous gas. Semiconducting metal oxides are the good candidates due to their low cost, high sensitivity, fast response, relatively simplicity of use and ability to detect a large number of gases. Applications of chemical sensors include environmental monitoring, automotive applications, emission monitoring, and aerospace vehicle health monitoring. It also outlines the advantages and disadvantages of each sensor for gas sensing application

Keywords: Gas sensors, Metal oxides, Semiconductor.

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1) Introduction:

Currently there is a flourishing world-wide interest in 'nanoscience' research which attempts to make and organize objects on the nanometer length scale, and also to understand the evolution of the bulk properties from the molecular properties in this region. Continued efforts in this field may lead to the development of novel materials with technologically important properties [1]. Nanocrystalline materials are distinguished from the conventional polycrystalline materials by the size of the crystallites. Nanocrystalline materials are single-phase or multi-phase polycrystals, the crystal size of which is of the order of a few (typically 1-100 nm) nanometers in at least one dimension [2].

Five types of material's state (differing by its structural properties) are : amorphous state, glass-state, Nanocrystalline state, polycrystalline state, and single crystal state. Nano- and polycrystalline materials have found the greatest application in gas sensors. A high specific surface area can take great advantage for the development of high-sensitive gas sensors. Amorphous and glassy materials are not stable enough at higher temperatures. Single crystalline and epitaxial materials have maximum stability of characteristics. One-dimensional metal oxide nanomaterials, such as nanobelts, nanorods, nanowires and so on, have excellent crystallinity and clear facet. At present, various kinds of one-dimensional nanomaterials such as $ZnSnO_3$, $CdSnO_3$, $NiSnO_3$ etc. were synthesized as nanowires, nanotubes, nanospheres, nanorods, and nanobelts.

As a famous multifunctional material, zincstannate ($ZnSnO_3$) has attracted considerable attention due to its potential applications in the fields of photo-electrochemical device [3], photocatalyst [4] and gas sensor [5]. The properties of nanocrystalline materials are very often superior to those of conventional polycrystalline coarse-grained materials. They exhibit increased strength, hardness, enhanced diffusivity, improved ductility/toughness, reduced density, reduced elastic modulus, higher or lower electrical resistivity depending on the material, high surface to volume ratio, increased specific heat, higher thermal expansion coefficient, lower thermal conductivity, superior soft magnetic properties, etc., in comparison to conventional coarse-grained materials.

2) Sensors

The sensor is the device, which senses the input signal. Now a day, there is a general opinion in both scientific and engineering communities that there is an urgent need for the development of cheap and reliable sensors for control and measuring systems, for automation of services and for industrial and scientific applications. For the development of the sensors, interest has been increased to study the sensing principles, simulation of systems and the structure investigations of most suited materials and proper choice of technology. The Physical changes in sensor active film may be thick or thin are transduced into electrical signals explained by [6] given in Table 1.

Table 1. The physical property and sensor device

Physical Changes	Sensor Devices
Electrical Conductivity	Semiconductor Gas Sensor
Mass	Piezoelectric sensor, Quartz crystal microbalances(QMB), surface acoustic wave(SAW), micro cantilevers
Optical Parameters: SPR, Reflection, Interferometry, Absorption fluorescence, Refractive index, Optical path length	Optical sensor (Fiber optic or thin film)
Work function(electrical Polarization)	MOSFET sensor: diodes, transistors, Capacitors
Heat or temperature	Catalytic gas sensors: Seebeck effect,

	Pellistors, Semistors
Electromotive force or electrical current in a solid state electrochemical cell	Electrochemical gas sensors: Potentiometric

2.1 Need of sensors:

The sensors are required basically for measurement of physical quantities and for use of in controlling some systems. Presently, the atmospheric pollution has become a global issue. Gases from auto and industrial exhausts are polluting the environment. The gases like LPG, NH_3, H_2, Cl_2, CH_4, H_2S, and CO_2 etc., have to be controlled for the healthy survival of the living beings. Thus, there is an increasing concern about minimization of the emission of autointoxication and also to reduce emission of such unburnt hydrocarbons from automobile and industrial exhausts. In order to detect measure and control these gases, one should know the amount and type of gases present in the ambient. Thus, the need to monitor and control these gases has led to the research and development of a wide variety of sensors using different materials and technologies.

2.2 Semiconductor Metal Oxide Sensor

The principal of operation of semiconductor metal oxide sensors is based on the change in conductance of the oxide on interaction with a gas and the change is usually proportional to the concentration of the gas. There are two types of metal oxide sensors: n-type (SnO_2, ZnO, TiO_2, Fe_2O_3 etc.) which respond to reducing gases and P-type (NiO, Co_2O_3) which respond to Oxidizing gases [7]. The sensors are applicable for air quality control, monitoring and detection of air pollutant hazardous gases. Therefore study of gases is necessary for research. Gases are classified as Inorganic and Organic gases, Inorganic class includes the oxides of carbon, sulfur, nitrogen and other gases like H_2S, NH_3, Cl_2, HF, etc. Organic class includes the hydrocarbons CH_4, C_2H_6, C_3H_8, C_2H_4, C_8H_{18}, Formaldehyde, vapors of acetone, alcohols, organic acids etc. Vapours of petrol, diesel, LPG and CNG are gases containing volatile organic compounds. Further they are classified as reducing gas like H_2, CH_4, CO, C_2H_5, H_2S [8]. Resistance drops by exposure of these gases on n-type material and increases when exposure on p-type material. P-type sensors responds to Oxidizing gases like O_2, NO_2 and Cl_2 .It is summarize in Table 2.

Table 2. Type of material, oxidizing gases and reducing gases

Classification	Oxidising Gases	Reducing Gases
n-type	Resistance increase	Resistance decrease
p-type	Resistance decrease	Resistance increase

General reaction mechanism on film surface is summarized by following equations

$$1/2\ O_2 + e^- \rightarrow O^- (s)\text{------------------------------}(1)$$

$$R\ (g) + O^-(s) \rightarrow RO\ (g) + e\text{-----------------------}(2)$$

Where, e is an electron from the oxide.

R(g) is the reducing gas

g and s are the surface and gas, respectively.

3. Environmental Hazardous Gases

A summary of physical property, source of emission, toxicity and threshold limit value of environmentally hazardous gases reported by American Conference of Government Industrial Hygienists are shown in table 3. (TLV) is defined as maximum concentration of chemical allowable for repeated exposure without producing adverse health effects.

Gas concentration is also important factor for gas sensors. Concentration levels of typical detectable gas components are summarized as follows.

Table 3. The physical property, source of emission, toxicity and threshold limit value of environmentally hazardous gases.

Gas	Physical property	Source of emission	Toxicity	TLV	References
NO_2	Reddish brown gas with pungent and irritating odor able to form gases nitric acid and toxic nitrates	Produced by all combustion gas in air produce from the trasportationsector and industrial processes	Irritating the lungs, respiraratory infection, degradation of rubber, damage tree and crops, resulting insubstantial losses when chemically transform to nitric acid ,irritating eyes ,etc	3 ppm	Air Quality control Ministry of Environment
H_2S	Colorless, toxic and flammable gas, Smell like rotten eggs	Occurring naturally incrude petroleum, natural gases, hot sprine, produced from bacterial break down of organic matters or waste produced by human and animal etc.	Damage in breathing system	10 ppm	Kaur et al.
CO	Colorless, odorless,	A by product of the incomplete burning	Preventing oxygen from being absorbed into the blood	50 ppm	Hazard fact sheet #1

	tasteless and non irritating gases	gasoline , wood, coal, oil, propene or any other substance that contains carbons, produced whenever combustion occurs	stream. Without sufficient oxygen in the blood stream, vital organs with stop function		
NH_3	Colorless gas with pungent order	Produced by the heating by the decomposition of animal manures	Irritates the eye at levels in the range of 20-50 ppm	25 ppm	www.en.wikipedia.org/wiki/Ammonia
CO_2	Colorless and odorless gas	All open flame, non vented space, Heater also contribute CO2 to the surrounding air as one of the product of combustion can created	Can create an oxygen defienceincyand asphyxiation or suffocation	5000 ppm	www.eoearth.org-article carbondioxide
CH_4	Colorless, odorless gas and combustible gas	Generated by an aerobic digestion of organic material and if stored can be used as a fuel source for internal combustion engines	Non toxic	1000 ppm	www.eoearth.org/article/methane
SO_2	Lighter than air Invisible gas with a nasty sharp smell	Industrial activity as a main source	Irritates the nose throat, and airways to cause coughing, wheezing, shortness of breath etc.	5ppm	Air quality fact sheet

4)Measurement of gas sensing performance parameter

The transducer converts this energy into a useful electrical signal corresponding to analytical change. It further classified into physical and biochemical sensors. In order to characterize sensor performance a set of parameters is used. The most important parameters and their definitions are listed below. [9]

- **Gas response:** is defined as the change conductance the sample on exposure to gas to the original conductance. It is given by the relation

$$G_g - G_a \qquad \Delta G$$

S = -------------- = ------…………………………….. (3)

G_a G_a

Where, Ga is the conductance of sensor in air,

G_g is the conductance of sensor in presence of gas.

- **Selectivity:** The response of the sensor to a specific gas in the mixture of gases is the selectivity.
- **Response time:** The time taken by the sensor to attain the 80% of maximum change in resistance on exposure to the gas is response time.
- **Recovery time:** The time taken by the sensor to roll back to 80 % of its original resistance is the recovery time.
- **Stability:** It is the ability of a sensor to provide reproducible results for a certain period of time. This includes retaining the sensitivity, selectivity, response and recovery time.
- **Detection limit:** It is the lowest concentration of the analyte that can be detected by the sensor under given conditions, particularly at a given temperature.
- **Dynamic range:** It is a analyte concentration range between the detection limit and highest limiting concentration.
- **Linearity:** It is the relative deviation of an experimentally determined calibration graph from ideal straight line.
- **Resolution:** It is the lowest concentration difference that can be distinguished by sensor.
- **Working temperature**: It is usually the temperature that corresponds to maximum sensitivity.
- **Life cycle:** It is the period of time over which the sensor will continuously operate.

All of these parameters are used to characterize the properties of a particular material or device. By Literature review highlights the ideal chemical or other types of sensor would posses high sensitivity, dynamic range, good selectivity and stability, low detection limit, good linearity, fast response and recovery time.

5) Brief Review of Literature:

Nanocrystalline perovskite materials exhibit many interesting and intriguing properties from both the theoretical and the application point of view. These compounds are used as sensors and catalyst electrodes in certain types of fuel cells and are candidates for memory devices applications.

Jiaqiang Xu, et al (2006) reports [10] the preparation and gas sensing characteristic of $ZnSnO_3$. The perovskite structure $ZnSnO_3$ was prepared by hydrothermal process directly. Its crystal structure and ceramic microstructure were characterized by X-ray diffraction and transmission electron microscopy and scanning electron microscopy. Its grain size is about 500 nm, and homogeneous as well as monodispersive in shape. Furthermore, the gas sensing properties of the materials were tested in static state. It is found that the sensors have good sensitivity and selectivity to H_2S.

Tong Zhang et al (2009),[11] Hollow $ZnSnO_3$ nanocubes with peculiar cage- and skeleton-like architectures are successfully synthesized by a simple hydrothermal process at 180 ^{0}C for 12 h . These $ZnSnO_3$ nanostructures exhibit almost uniform cubic structures with side length of 200–400 nm. The gas sensor based on these $ZnSnO_3$ nanostructures exhibits high response and quick response-recovery to ethanol and HCHO, which also shows superior sensitive performance compared with the results of sensor based on solid $ZnSnO_3$ nanocubes.

Chongmu Lee et al (2012) studied [12] on $ZnSnO_3$ one-dimensional (1D) nanostrutures were synthesized by thermal evaporation. The morphology, crystal structure and sensing properties of the CuO -coated $ZnSnO_3$ nanostructures to H_2S gas at 100 ^{0} c were examined. The diameters of the CuO nanoparticles on the nanorods ranged from a few to a few tens of nanometers. The gas sensors fabricated from multiple networked CuO-coated $ZnSnO_3$ nanorods exhibited enhanced electrical responses to H_2S gas compared to the uncoated $ZnSnO_3$ nanorod sensors, showing 61.7-, 49.9-, and 31.3-fold improvement at H_2S concentrations of 25, 50, and 100 ppm, respectively. The response time of the nanorod sensor to H_2S gas was reduced by the CuO coating but the recovery time was similar.

Patil et al (2014) work on [13] nanostructured $ZnSnO_3$ thin films were prepared onto preheated glass substrate by a spray pyrolysis technique using water soluble Zinc chloride and Stannic chloride as precursors. The crystallinity of the prepared samples was analyzed by X-ray diffraction spectroscopy. The X-ray diffractogram of as prepared thin film clearly indicated the stichiometric and pervoskite nanostructured nature of $ZnSnO_3$. The TEM image shows few nanorods along with fine particles of pervoskite $ZnSnO_3$. The sample showed selective response to H_2 gas among the various gases such as LPG, hydrogen, ethanol, chlorine, carbon dioxide and ammonia. The dynamic response of $ZnSnO_3$ pervoskite thin film sample is presented. The pervoskite oxides were used as potential gas sensing material for their stability in thermal and chemical atmospheres .

I. Saafia, et al (2016), [14] deals with some physical investigation on SnO_2–$ZnSnO_3$ ceramics grown on glass substrates at different temperatures (450^{0}C and 500^{0}C). Structural and optical properties were investigated using X-Ray diffraction (XRD), Raman, infrared (IR) absorption (FTIR), UV–visible spectroscopy and Photoluminescence (PL) techniques. XRD results revealed the existence of a mixture of SnO_2–$ZnSnO_3$ phases at different annealing temperatures .

Wu et al. (2002), [studied the electrical characteristics of some perovskite oxides such as $NiSnO_3$, $ZnSnO_3$ and $CdSnO_3$ [15].

The SP technique is useful for the production of thin films of simple oxides, mixed oxides, metallic spinel type oxides, group I-VI, II-VI, III-VI, IV-VI, V-VI, VIII-VI binary chalcogenides, group I-III-VI, II-II-VI, II-III-VI, II-VI-VI and V-II-VI ternary chalcogenides [16]. These thin films have great technological importance owing to their potential applications in photoectrochemical cells, solar selective and decorative coatings, optoelectronic devices and thermoelectric coolers.

6) Conclusions

Gas sensor films, prepared from nanocrystalline thin films, offer grain sizes, where depletion layer has almost the same dimensions as the particle radii, and consequently electrical conduction is predominantly grain controlled. Porous films composed of nanoparticles with diameter between 6 and 20 nm showed improved sensitivity and high gas selectivity due to increased surface area to volume ratio. Thin films composed of nanoparticles showed a strong dependence of the gas concentration on mobility of charge carriers. Chemisorbed O- species at the surface acts as scattering centers and resist the movement of charge carriers. Adsorption of reducing gas results in the decreased or elimination of these scattering centers. This can be achieved in this research work undertaken. Nano-based gas sensor showed novel improvement in the characteristics of sensor. Our aim is to achieve the good characteristic gas sensor.

Acknowledgement

The authors are thankful to the Principal, Shri. V.S. Naik. Art, Commerce, Science College, Raver, for providing laboratory facilities for this work.

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