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Tin Doped Gas Sensors in Semiconductor Metal Oxide Form and Their Scientific Applications: A Review

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ABSTRACT: This article imparts the contribution for Semiconductor Metal Oxides as tin doped gas sensors in environmental applications by providing information in the form of statistical base and shares knowledge to technicians for finding and protecting the environment from different gases like CO, CO_2, H_2S, NH_3, Marshy Gas Methane, LPG and many other pollutant gases. It also focused on different characteristics of single gas sensors along with composite form at different temperatures in controlled way. It has been proven to be that gas sensors made up with different material in composite form is more reliable than gas sensors made up with single one for environment gases.

Keywords: Environment; gas sensor; pollutant gas; statistical base; semiconducting metal oxide.

INTRODUCTION: In the era of basic science the term sensor plays a vital role that keeps its importance with abreast of time and technology. The term sensor has been mostly used since 1980. Metal oxides are extensively used in various fields such as solar cells, optical devices and oxidation catalysts. Present paper will focused on the role of its one apostle a gas sensors made up with thick film technology, whose thickness depends on deposition parameter used. A good sensor is always defined in terms of speed, selectivity, sensitivity and stability. It is also can be expressed in terms of linearity and repeatability. Gas sensors especially chemical sensors have found the extensive applications in the process control of industries and environmental monitoring. Chemical sensor is the matrix of Physical, Chemical and Biochemical phenomenon. Chemical sensor always made up of two important components; one of them is sensor itself and analyzer [1]. Sensing technique has been adopted in instrumental forms which on the other hand rely on type of pollutants, their concentration and state of occurrence. The chemical technique like amperometric or potentiometric is used to detect the electro active pollutants such as NO_x, H_2S, SO_2, CO etc. For these purpose proper sensing cells are developed with electrode catalyst and membrane permeability. With the help of these technique reactant concentration can be measured up to limit of 100ppb. SMOs like SnO_x or metal filaments like platinum produce current when pollutant gases are oxidized on them. But these chemical techniques fail because of lack of selectivity though sensitivity is quite high. There are numerous methods which are adopted for the development of sensors such as thick and thin type, standard methods of semiconductor device technology, micro-electromechanical systems and nano technology. Thin films are deposited by Physical vapor deposition, Sputtering deposition, Molecular beam epitaxy, Chemical vapor deposition, Metallo-Organic Deposition. Thick films are prepared with the aid of Screen printing technique [2]. Thin and Thick films made up with oxides of different materials like tin, titanium, indium and zinc are found to be less sensitive than their counterpart of their additives likely to be with different pollutants such as CO, CO_2, NH_3, Ethane, Ozone, Methane, LPG and many more. Among all these gases CO_2 is most dangerous gas in world because of its influence in global warming against human life, it is global alarm for vivo and vitro. The CO_2 concentration was found to be 280

ppm in the midst of 1800 century but industrial revolution have increased its concentration and it was reach up to 370 ppm in 2001. It is rising by 1.5 ppm per year. Marshy and wetland is the main source of methane. Now days its concentration reach up to 1.4 ppm which is a thing of concerning. In the last 200 years the proportion of ozone has doubles near earth surface [3]. Gas sensors are act as Detectors for detecting and controlling environmental gases even in parts per million gas concentration level.

Environmental gases those acts as Pollutants: Environment is the form of atmospheric condition. Environment is the sum of total water, air and land interrelationships among themselves also with the human being, other living organisms and property [4]. The components of environment are air, water and soil. These components are now becoming the house of pollutants because of advancement of agriculture, Industrial revolutions, Mining and Transportation (viz. road, sea and air etc.) Most of the gases which acts as pollutants are hydrogen sulfide, ammonia, nitrogen dioxide, nitric oxide, carbon monoxide, carbon dioxide, vapors of petrol, diesel, sulfur dioxide, sulfur trioxide, LPG, CNG, dust particles, ozone, vapors of king of chemical sulfuric acid, oleum vapors ($H_2S_2O_7$) emerging from chemical industry, chlorine, methane, ethane, propane, ethene, propene, benzene, formaldehyde, alcohol vapors, acetone vapors, particulate matters like dust, smoke, ash, lead, carbon etc., inflammable gases like hydrogen, ethanol have made hazardous effect on human health and environment[4-5].

About $SnO_2$and Its Composites as a Gas Sensor: In 2004, B. Licznerski [6] point out that with time man have made significant efforts to overcome problems created in environment and minimize the hazardous and dangerous effects by inventing the remedy parameters in science and technology. Man have made achievements in microelectronics preparing low-cost semi-conductive sensors. Man consistently construct, develop a sensors in massive and large production since last three-four decades based on gas sensitive materials changing its resistance and/or impedance when hazardous substances appear in nature. First successful SMOs were made metal oxide ZnO, TiO_2, Fe_2O_3, Al_2O_3, Y_2O_3 and SnO_2. In 1997, B. Licznerski et al. constructed a sensor of tin dioxide platinum black using raw cermet composition for methane in presence of CO gives the best response at temperature 560^0C avoiding *cross-sensitivity* of SnO_2 [7, 8]. Similar observations have made in 2001 by B. Licznerski et al, for SnO_2 –Rh thick films annealed at 600^0C for 5 Hours. The sensor conductance decreases in presence of reducing gases [9]. In 2003, B. Licznerski et al. made thick films of SnO_2-RhO_2 sensitive to methane and insensitive to the presence of CO [10]. Numerous Semiconducting Metal Oxides (SMOs) materials have been reported to be usable as sensor, among all SnO_2 widely used as gas sensor. It is mostly studied because of its interest in both application as well as in fundamental research. It has remarkable optical and electrical properties. All SMOs are non-stoichiometric structure so free electrons originating from oxygen vacancies contribute to electrical conductivity. Tin oxide has wide band gap (3.6 eV) having its conductivity depending upon oxygen vacancies that acts as donors. The gas sensing properties of SnO_2 semiconductor thick film have found to be strongly depends on the method of processing. Thick films are used to prepare tin oxide gas sensors since gas sensing properties depends on the surface of material and gases are always adsorbed and react with surface films. Even these undoped SnO_2 thick film is found to be suitable for LPG sensor at room temperature. In 2012, Shukla T [11] reported screen printed thick solid SnO_2 films are tetragonal crystallite in nature with size in the range of 14-30 nm. For LPG average maximum sensitivity of film was 37 MΩ/Min for 5 vol. %. Sensor responses as a function of exposure and response times were also estimated and maximum sensor response were found 273 and 312 for 4 and 5 vol % of LPG respectively. So SnO_2 gas sensor can be used in domestic, industry purposes in large scale. In 2011, Mohammad abadi et al. [12] prepared a screen printed SnO_2/Pt thin film laser ablated gas sensor array was developed in 10×10 mm^2 space on alumina substrate at room temperature deposited with 1064 nm Nd-YAG laser with a power of 0.7 J/s at different deposition time 2, 5 and 10 min, in an atmosphere containing 0.04 mbar (4 kPa) of oxygen. The array was moderately sensitive to sub ppm of the applied species and shows a great sensitivity to the applied gases such as methanol, isopropanol, acetone and wood smoke at concentrations above 10 ppm with a response time below than 10 second. It is observed that at lower concentration of the applied species similar differences of the sensing values were observed, while at higher concentration of the applied species greater differences of the sensing values were observed, while in 1000 ppm of the applied species the $Sn_{10}Pt_2$ shows a remarkable sensing value in presence of all species, except for the wood smoke, compared to the sensing value of other sensors of the array at operating temperature 200^0C. Higher concentration of Pt nanocrystals into the Sn sites makes a better trap for CO and CO_2 species, resulted in greater sensing values especially at higher concentration of the applied CO and CO_2. In 2008, Borse R.

Y. and Garde A.S. prepared thick SnO_2 solid films with thickness 10 µm-13µm on alumina substrate by standard screen printing technique, observed that SnO_2 shows decrease in resistance with increase in concentration of H_2S gas obeying negative temperature coefficient of resistance thereby semiconducting property with highest sensitivity at 350^0C is 0.4 at 600 ppm when films are annealed at 680^0C for 30 min. The gas sensing mechanism was adsorption controlled [13]. In 2004, Il Jin Kim et al. [14] explicated that thick film SnO_2 loaded with CeO_2 and PdO_x sensor was fabricated for CO gas in the wt. % ratio 94:5:1 respectively. The nano-crystalline powder of SnO_2-CeO_2-PdO_x composites synthesized by sol gel method were screen printed on alumina substrate, fabricated sensor also even tested for H_2, CH_4, C_3H_8, C_2H_5OH, NO_x and SO_2. The CO sensor gives the response even at 40 ppm the working temperature range between 120 and 180^0C with interference of other gases and sensitivity 130 for maximum 400 ppm for CO sensor. In 2006, Kiran Jain et al. [15] belonging to National physical laboratory of Delhi showed that reduction in grain size thick film SnO_2 gas sensor for LPG on Al and Ni doping, also gas sensitivity is affected by not only by additive but the way it is added into the sensor material. The results on resistance, response and recovery time were explained in terms of n-p junction formation between SnO_2 and NiO, which increases the depletion barrier height. In 2016, [16] Nadaf L.I. et al, prepared thin films of SnO_2 by Co-precipitation method with and without (23.782 nm) surfactants. They reported that size of SnO_2 effectively decreases using surfactants like lauryl alcohol (21.2 nm)and Triton-X100 (5.8 nm) there by find application in photovoltaic, chemical gas sensing.

Table 1: LPG and other gases used for sensor materials with different operating temperature, concentration and gas response.

Material	Temp.	Sensitivity	Concentration	Refs.
SnO_2	600	10.5	2000 ppm Ethanol	[6]
SnO_2	450	7.8	40 ppm Ethanol	[6]
SnO_2	450	11.5	300 ppm	[6]
SnO_2-Pt	560	High	CH_4 in CO	[7]
SnO_2-Rh	600	High	CH_4 in CO	[7]
SnO_2-RhO_2	R.T	High	CH_4 in CO	[10]
SnO_2	R.T	273	4% vol LPG	[11]
SnO_2	R.T	312	5% vol LPG	[11]
$Sn_{10}Pt_2$	200	4.5	10 ppm Ethanol	[12]
$Sn_{10}Pt_2$	200	2.7	10ppm Xylene	[12]
$Sn_{10}Pt_2$	200	3.1	10 ppm Methanol	[12]
$Sn_{10}Pt_2$	200	6.1	10 ppm Isopropanol	[12]
Sn10Pt2	200	6.1	10 ppm Acetone	[12]
$Sn_{10}Pt_2$	200	3.2	10 ppm Wood Smoke	[12]
$Sn_{10}Pt_5$	$Sn_{10}Pt_2$	2.4	10 ppm Ethanol	[12]
$Sn_{10}Pt_5$	200	2.5	10 ppm Xylene	[12]
$Sn_{10}Pt_5$	200	3.1	10 ppm Methanol	[12]
$Sn_{10}Pt_5$	200	3.5	10 ppm Isopropanol	[12]
$Sn_{10}Pt_5$	200	5.4	10 ppm Acetone	[12]
$Sn_{10}Pt_5$	200	4.4	10 ppm Wood Smoke	[12]
SnO_2	350	0.4	600 ppm of H_2S	[13]
SnO_2-CeO_2-PdO_x	180	130	300 ppm CO	[14]

DISCUSSION AND CONCLUSION: Development in technology perks the environment and human safety. The importance of gas sensor research is highly increasing due to connectivity to social issues and environmental problems. The scope of fabrication of gas sensors has been grown up simply means of selection of functional sensing materials, addition of additives, and their varying doping concentrations. Table 1 indicates SMO composites shows better sensitivity and gas response than their single counterparts.

Abbreviations: SMO- Semiconducting metal oxide. LPG- Liquefied petroleum gas.

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