Chapter-5

SnO_2 as a Gas Sensing Material

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This chapter discusses about gas sensors in general and metal oxide gas sensors in particular. SnO_2 is one of the most exploited materials in the field of gas sensors. Selection of SnO_2 as the sensing material and the properties of SnO_2 along with its applications are also presented. The relevant work, which had a substantial influence in the field, is discussed.

1. INTRODUCTION

A change in parameter is detected and converted it into a readable signal by a sensor. A sensor works on the principle that a physical condition like position, displacement, distance, speed, acceleration, vibration, angle, angular speed, torque, pressure, force, temperature, humidity, flow, gas and liquid concentrations, electromagnetic radiation, magnetic field strength, electrical voltage and current, and many more is detected and converted to a measurable response. The phenomena, which are detected, might be

biological, chemical, electric, electromagnetic, heat/temperature, magnetic, mechanical motion, optical or radioactive. The output is in the form of a human readable signal. Hybrid sensors has gained pace in its use and are integrated in electronic systems to monitor, optimize and control the functions of a system or environment. Device operation needs idealised condition, which may be achieved with the use of sensors, which sets the benchmark. The common outputs, which can be measured as an output, are listed in table 1. A sensor does not operate on its own and has a set of components involved such as signal conditioners, signal processors, memory devices, data recorders and actuators.

Sensors are a part of our day-to-day routine. Devices such as thermometers, barometers, mobile phones, touch-sensitive elevator buttons (tactile sensor), table lamps, speedometers and various other devices are sensors. Technology has advanced and hence the reach of sensors has gone beyond these traditional fields. Sensors are used in manufacturing and machinery, airplanes and aerospace, cars, medicine, and robotics apart from the general day to day use.

Sensors have specific property, which segregates them.Temperature sensors involve thermometers, thermistors and thermocouples. Pressure sensors are components like fibre optic systems, vacuum systems, elastic liquid based manometers. Flow sensors involve measurement of differential pressure, positional displacement and thermal mass. Differential pressure, ultrasonic radio frequency, radar and thermal displacement can be measured using level sensor. Resonant mirror, electrochemical systems, surface plasmon resonance are biosensors. Charged coupled devices (CCD) are image

sensors. Gyroscopes and accelerometers are motion sensors. Other kind of sensors such as gas sensors, moisture/humidity sensors, tilt sensors, force sensors also exists.

Table 1: Detection parameters used in sensors

Stimulus	Quantity	Sensor
Acoustic	Wave (amplitude, phase, polarization), Spectrum, Wave Velocity	Surface acoustic wave sensor
Biological and chemical	Fluid Concentrations (Gas or Liquid)	Gas sensors
Electric	Charge, Voltage, Current, Electric Field (amplitude, phase, polarization), Conductivity, Permittivity	Ammeter, Voltmeter
Magnetic	Magnetic Field (amplitude, phase, polarization), Flux, Permeability	Compass
Optical	Refractive Index, reflectivity, absorption	Binoculars
Thermal	Temperature, Flux, Specific Heat, Thermal Conductivity	Thermometer
Mechanical	Position, Velocity, Acceleration, Force, Strain, Stress, Pressure, Torque	Flow meter, pressure gauge

New age sensors are bundled system, which measures a change and converts them into readable signal. For such purpose a transducer is employed that converts a measured physical quantity into an electrical domain signal in the form of change in capacitance, resistance, inductance or charge of the sensing element. The voltage source for such devices is either AC or DC depending on the application.

A sensor is desired to have some important attributes like sensitivity, stability, repeatability, response time, durability, non-toxic, easy operation, small size, easy fabrication and relative temperature sensitivity. To be a commercially viable and affect sensor these properties must be fulfilled for a range of values. The sensor must be reusable and hence should recover the original state on repositioning it a test free environment. The output obtained stands valid only if repetition is displayed.

2. GAS SENSORS

Broadly speaking sensors can be chemical sensors or physical sensors. From the concentration of a specific sample component to total composition analysis, a gas sensor changes theses chemical information into an analytically useful signal. For a safe and pollution, free environment a gas sensor plays a vital role as it monitors the surroundings for harmful gases. Combustible, flammable and toxic gases and oxygen depletion can be detected with its application. Gas sensors involve infrared point sensors, infrared imaging sensors, ultrasonic sensors, electrochemical gas sensors and semiconductor sensors. Broadly, gas sensors are utilised to detect three conditions:

a. Detecting combustible gases in the sorroundings that can cause a fire outbreak or explosion.
b. Detecting oxygen for having a breathable environment and control of combustion
c. Detecting toxic gases and safeguard and safe exposure to the environment.

2.1 Types of Gas Sensors

Gas sensors can be categorized as acoustic wave based gas sensors, capacitance based gas sensors, optical gas sensors, calorimetric gas sensors, metal oxide based gas sensors and electrochemical gas sensors (Fig. 1).

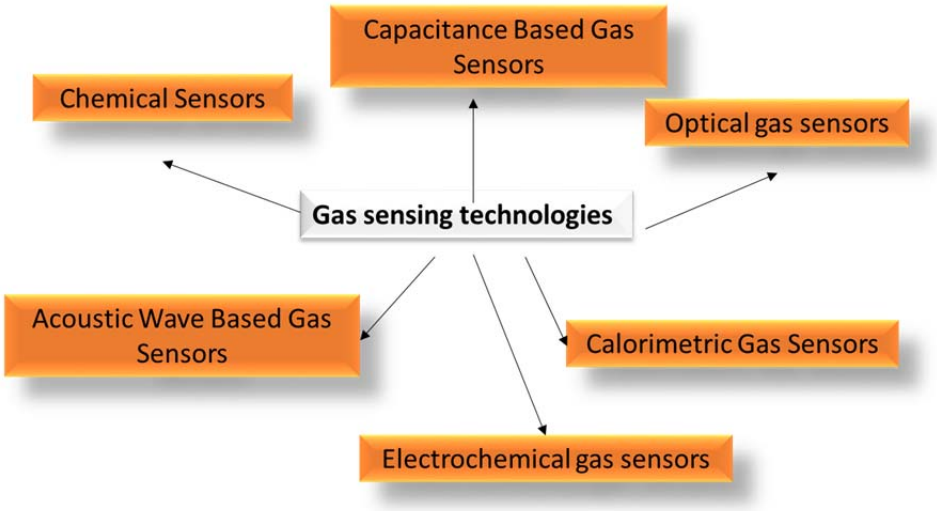

Fig. 1: Gas sensing technologies

In capacitance based gas sensors, the change in dielectric constant of films between the electrodes as a function of the gas concentration is measured. The capacitive sensor contains inter-digitated electrode structures, have a capacitor setup to monitor changes of the dielectric coefficient of the film. Whether the capacitance will increase or decrease, depend on the dielectric constant of the film with the introduction of gas. Acoustic wave based gas sensors are basically sound detectors. A piezoelectric material is employed which is connected to one or more transducers. The acoustic waves generated because of the gas pressure exerted on the piezoelectric material

ISBN: 978-93-85822-38-4

is used to measure properties, processes, or chemical species in the gas phase, liquid phase, vacuum or thin solid films. Calorimetric gas sensors work on the principle of change in temperature at catalytic surfaces. It consists of a surface of a film of a catalytically active metal (e.g. Platinum, Palladium or Rhodium). When a volatile gas is burnt heat is generated due to the combustion. This heat is balanced by a reduction in the electrical heating power and this power consumption indicates the concentration of gas. Optical gas sensors employ methods like ellipsometry, spectroscopy, interferometry which determines the quantity such as refractive index, absorbance and fluorescence properties. Electrochemical gas sensors consist of chemical reactants (electrolytes or gels) and two terminals (an anode and a cathode). Anode is responsible for oxidization process and cathode is responsible for reduction process. When current is generated because of positive ions flow to the cathode and the negative ions flow to the anode, we can find reducible gases (such as oxygen, nitrogen oxides and chlorine) at the cathode and oxidizable gases (carbon monoxide, nitrogen dioxide, and hydrogen sulphide) at the anode.

2.2 Metal Oxide Based Gas Sensor

Metal oxide based semiconductor are designed using materials like SnO_2, TiO_2 and ZnO and their doped versions. These devices are based on the adsorption of gas molecules on the surface of the detecting material. The adhesion of the molecules to the thin layer of sensing material is converted into a readable electrical signal. The adsorption of the gas molecules can be either chemical (chemisorption) or physical (physisorption). In chemical

adsorption, the adsorbate and adsorbent share a strong bond and becomes a single entity. It is usually irreversible. In physical adsorption the lattice of the detecting material is weakly perturbed.

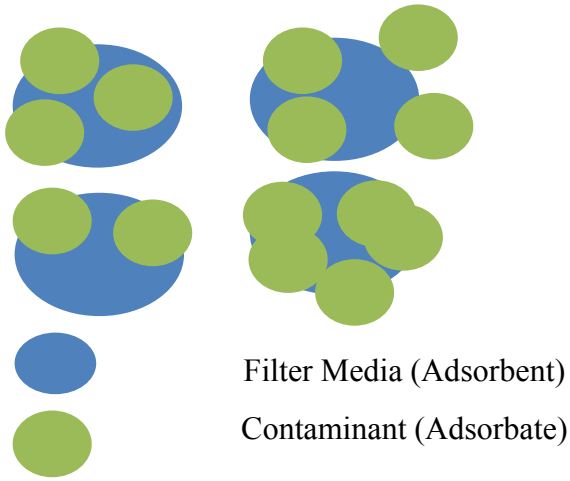

Fig. 2: Adsorbate and adsorbent interaction

The concentration of the gas in the vicinity can be measured. Each gas has a definite breakdown voltage which when applied the gas is ionized. The sensors identify the gases by measuring these voltages. The metal oxide contributes to the dissociation of gases into ions and complexes on the surface, which result in electron transfer. This electrical signal behaviour and detection depend on factors like chemical composition of the metal-oxide surface and its work function behaviour. A gas sensor performance is determined by the electron donor/acceptor properties of the test gas, adsorption coefficient, surface reactions and desorption of the gas at the later stage after detection. The oxygen vacancies on the surface of the sensing material are electrically and chemically active. The environment

where the gas is to be detected can be oxygen rich or might have charge accepting molecules and undergo a redox reaction. In presence of molecules like NO and O_2 near the vacancy sites, electrons are extracted and reduced in the conduction band thereby reducing the conductivity. Molecules like CO and H_2 reacts on the surface and releases captured electrons which result in raising the conductivity [1].

3. OXIDE STRUCTURES

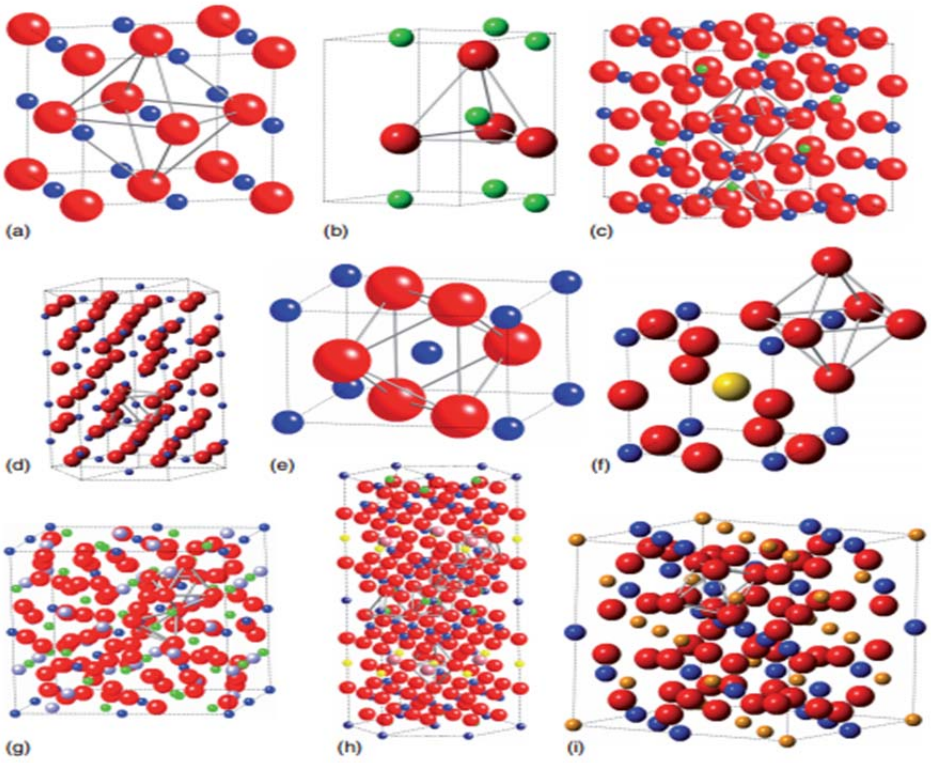

Fig. 3: Some common oxide structure types (a) halite, (b) wurzite, (c) spinel, (d) corundum, (e) rutile, (f) perovskite, (g) garnet (h) magnetoplumbite, and (i) pyrochlore

Oxides are omnipresent and oxygen being the most abundant of the elements available helps the cause. These are ionic compounds where the charged metal cations are embedded in a lattice of oxygen ions. In most cases oxygen forms a defective or defectless dense-packed lattice, either face-centered cubic (FCC) or hexagonal closed packed (HCP). The oxide structure can have various defects [2]. It can be a point defect that includes vacant oxygen or metal sites or presence of metal cations in the interstitial sites. In case of planar defects, the grain boundaries and missing planes of oxygen are observed. Defects contribute to the change of electronic, optical and magnetic properties of the metal oxides [3].

Some common oxide structures are halite, wurzite, spinel, corundum, rutile, perovskite, garnet, magnetoplumbite and pyrochlore (Fig. 3). The halite structure is composed of two interpenetrating fcc sublattices, with cations and anions alternating along [100] directions. The Wurzite structure is composed of two interpenetrating hcp sublattices. The spinel structure is based on an fcc array with 32 oxygen ions. Corundum (sapphire) structure is based on an hcp oxygen array, where the metal ions occupy 2/3 of the octahedral interstices. The rutile structure can be regarded as a distorted hcp oxygen array, where metal ion occupies ½ of the octahedral interstices. The perovskite structure is pseudocubic. Here the element along with the oxygen ions form an fcc lattice, and the metal ions occupy ¼ of the octahedral interstices, coordinated only by oxygen. Garnet structures like pyrope, $Ca_3Fe_2Si_3O_{12}$, have a big cubic unit cell containing 96 oxygen atoms. Magnetoplumbite structure has a tall hexagonal cell containing 76 oxygen

ISBN: 978-93-85822-38-4

ions. Pyrochlore is observed in mineral $Ca_2Nb_2O_7$. The structure is derived from that of fluorite and there are 56 oxygen ions in a cubic cell [3]

3.1 Tin-Oxide-Structure

Tin belongs to block P, period 5 and group 14 of the periodic table. The chemical abstracts service (CAS) no is 18282-10-5 and bears the electronic conFigureuration [Kr] $4d^{10}$ $5s^2$ $5p^2$. The two stable oxide forms of tin are stannous (tin II) compounds and stannic (tin IV) compounds. Stannous oxide (SnO) is crystalline and blue-black in color. The compound shows thermal stability till 385 ^oC in air and has a tendency to convert to stannic oxide (SnO_2) which is white in color and exists in the earth's crust as a mineral cassiterite. SnO_2 contains 78.76% tin and 21.21% oxygen. SnO is used in chemical industries for making tin salts, which are used in reagents. SnO_2 acts as an oxidation catalyst and is employed in the petroleum industry.

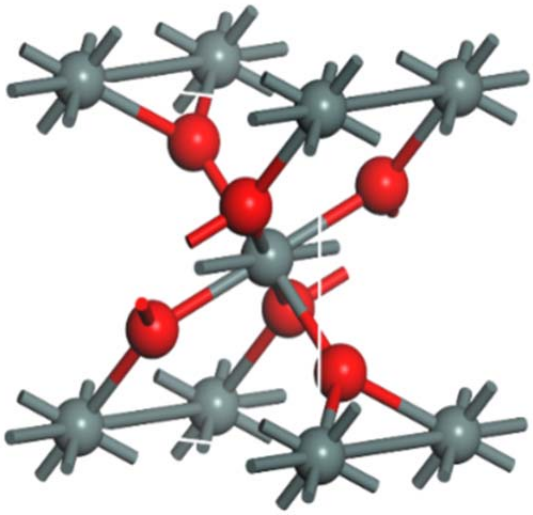

Fig. 4: Structure of SnO_2 (Grey –Tin, Red - Oxygen)

ISBN: 978-93-85822-38-4

The crystalline SnO_2 has a tetragonal rutile structure and is iso-structural. It belongs to the space group $P4_2/mnm$ and point group D_{I4}^{4h}. The lattice parameters are a = b = 4.738 Å and c = 3.188 Å. Each of SnO_2 unit cell consists of four oxygen atoms and two tin atoms. A linear chain is formed along the c-axis (Fig. 4). The structure is so formed that the oxygen ions acts as a bridge, which connects the chains. It also axially co-ordinates to a cation in the neighbouring chain [4]. Tin oxide comes under the category of transparent conducting oxides (TCOs) and finds application in electronic devices. Its combination of electronic and optical properties expands the horizon of its applications[5-11]. The properties of SnO_2 are being explored since 1950. Pure SnO_2 is a semiconductor having a direct band gap of 3.6 eV and an indirect band gap of 2.3 eV at 300K [5,12,13]. The gas sensors design in the present scenario is based on SnO_2 materials. The synthesized material is in the form of thin films, thick films and pellets. The non-stoichiometric form, SnO_x ($1<x<2$) also exhibits gas sensing properties [14,15]. The ion Sn^{2+} has a $5s^2$ electronic configuration. SnO_2 has the preferred growth direction along the planes (110) and (100). For bulk systems of SnO_2 the tin ions of ideal SnO_2 surface are in the lowest ionic state (Sn^{4+}). The surface bears a flat band which implies that the conduction and valence band are not distorted [16].

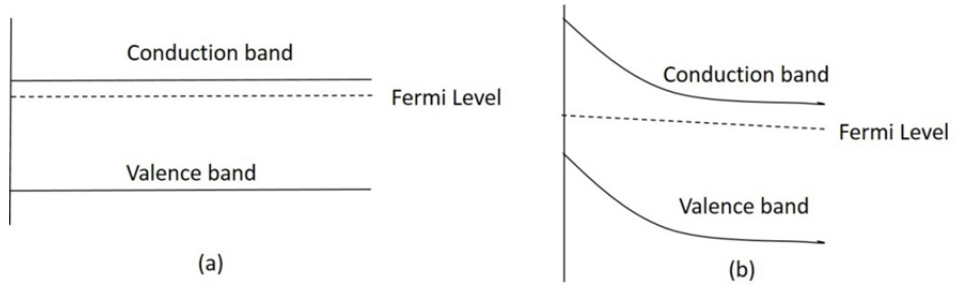

Fig. 5: (a) Undistorted Energy band diagram (b) Bending of bands due to adsorption of oxygen on surface

Due to the absence of the bending property of the conduction (Fig. 5) and valence band the thin film, as well the bulk material of SnO_2 bears similar electron transfer phenomenon between the bands.

3.2 Electronic band structure of SnO_2

The band structure of SnO_2 can be evaluated theoretically by density functional theory (DFT) calculation that is also reported in this thesis in details in chapter five. The band structure is calculated by plane-wave pseudopotential method. The generalized gradient approximation (GGA) represents the exchange-correlation energy of the electron gas. GGA and local density formalism (LDF) methods underestimate the band gap, which can be corrected using scissors operator. Robertson [17] estimated the band for the first time. This was followed by numerous other improved methods for the exact calculation of the band gap [18-20]. In the band diagram, the band gap is observed to be direct and consist of 96% Sn s state.

ISBN: 978-93-85822-38-4

4. PROPERTIES OF SNO_2

The conductivity of SnO_2 is a direct result of its non-stoichiometry[21-23]. The modulation of the conductivity can be achieved by controlling the carrier concentration in the form of doping. The conductivity can be varied depending on the end use from 10^{-6} S/cm [24] to $1.2x10^4$ S/cm [25,26].

Optically transparent solid materials are characterized to be electrical insulators. Conductivity is good only in few transparent solids like SnO_2 and In_2O_3[22,27]. SnO_2 films are 97% transparent in the visible range [28-30] and the resistivity is appreciably lower than that of semiconductors. The carrier density of SnO_2 is comparable to semimetals [27] and hence used as transparent electrical contact in flat panel displays and solar cells [27,31].

Table 2: Thermal properties of SnO_2

Property	Value
Heat of Formation	$1.9x10^3$ J mol^{-1}
Heat capacity	52.59 J mol^{-1} K^{-1}
Density at 300K	6.95 g cm^{-3}
Melting point	1630 ^oC
Boiling point	1800-1900 ^oC

The thermal properties are listed in Table 2. Wide band gap semi-conductors are capable of replacing the crystalline counterparts in TCO applications, as they possess low processing temperature and cheaper cost. The mechanical properties of SnO_2 can be modified for expanding its field of application by structural modification through doping or annealing at different temperature. Tin oxide films shows good adhesion to glass and

silicon substrate. Adhesion to glass substrate for crystalline thin film is greater than 300 kgF/cm^2 [32].

Semiconducting oxides like TiO_2, ZnO and SnO_2 shows good sensitivity towards gases [33,34]. At temperatures below 400 ^oC TCOs like ZnO and SnO_2 the chemisorption and physisorption phenomenon becomes active and influences the surface and grain boundary conductivity [35].

The field of spintronic demands dilute magnetic semiconductors (DMS) with high curie temperature. The magnetic property study of pure and doped SnO_2 have been explored a number of times [36-40]. The magnetic properties are explored at low temperature as well [41].

5. APPLICATIONS OF SNO_2

Transparent conducting oxide (TCO) finds major application in various fields like solar cells, flat panel displays, smart windows, touch screens, automotive applications, and transparent electronics and optoelectronic devices. SnO_2 belongs to the category of TCOs and has added application because of its properties. The magnetic properties of SnO_2 are explored in magnetic data storage and magnetic resonance imaging. It is used as catalysts, energy saving coatings, anti-static coatings, electrodes, gas sensors and resistors. The low toxicity of the inorganic compound is an added advantage of the material for wide range application. Anhydrous SnO_2 is used in high-qualityartware; where reflectance and abrasion resistance is essential. The use in ceramic industry is mainly because of the fact that it can accommodate foreign metal colourant ions in its structure. For electrical melting of glass, tin oxide is preferred as the electrode. SnO_2

containing CuO and Sb_2O_3 as the dopant for better conductivity is utilised in manufacturing lead crystal glass. Combining SnO_2 with vanadium, chromium, molybdenum, antimony, bismuth, phosphorus, copper, manganese, tungsten, platinum or palladium enhances its catalytic property, which in turn displays wide activity and selectivity. The catalytic and the electroconductive property of the material make it a major candidate for gas sensors. Such gas sensors are utilised in fire alarm system and in pollution monitoring environments. Anhydrous SnO_2 is used as putty powder for polishing marble, granite, glass and plastic lenses.

6. SNO_2 AS A GAS SENSOR

Gas sensors are used in industrial plants for methane detection [42-46], for detecting polluting gases from vehicles [47-51], medical field [52-55], air quality check [56-58] and environmental studies [59-62].

Gases can be sensed based on electrical property variation using metal oxide semiconductor, polymer, carbon nanotubes or moisture absorbing material. Gases can also be sensed depending on other changes like optical properties, acoustic properties or calorimetric changes. Some of the major parameters that must be evaluated in order to develop a good gas sensors are sensitivity (should detect low ppm of gas), selectivity (should detect different types of gases), response time (should detect gas in minimum time), energy consumption (should be minimum), reversibility (should be able to regain the original configuration when gas is removed) and fabrication cost.

Low cost and good sensitivity are the prime features of metal oxide semiconductors (MOS) which makes it a desirable candidate for fabrication of gas sensors. Non-transition and transition metal oxides can be used as gas sensors. Non-transition elements consists of only one oxidation state which is not suitable for gas sensing application [33]. On the other hand, transition metal oxides form various oxidation state. d^0 and d^{10} electronic configuration are used in the gas sensing phenomenon [63]. The d^0 configuration is present in transition metal oxides (TiO_2, V_2O_5, WO_3) and d^{10} exist in post transition metal oxides like SnO_2 and ZnO. Metal oxide semiconductors based gas sensors detect the gas based on the redox reaction between the oxide surface and the gas. This results in the change in the electrical resistance which can be detected by measuring the change in the capacitance, work function, mass, optical characteristics or reaction energy [63]

One of the most widely explored gas sensing material is SnO_2. It exhibits gas-sensing properties even in the non-stoichiometric form, SnO_x (x lies between 1 and 2) [14,15]. SnO_2 is n-type MOS whose change of electrical property is a function of pre-adsorbed oxygen ions on its surface. When gases like liquefied petroleum gas (LPG), methane (CH_4), carbon monoxide (CO) and other reducing gases[51,64] interacts with the surface of SnO_2 the resistance changes. SnO_2 works in the temperature range 25 ^oC to 500 ^oC and the temperature for detection of different gases are different [65]. This poses a selectivity problem if the difference in the detection temperature of the gases lies in a close range. A suitable dopant is hence preferable for promoting better selectivity within a small temperature range [33]. The

improvement of the sensing properties of the material with use of dopants, synthesis process, and structural changes is being constantly experimented with by various research groups. SnO_2 is used in bulk and as thick and thin films and porous pellets for gas sensing. The good gas sensing behaviour of the material is attributed to its high capacity to adsorb gaseous molecules. This enhances the surface reactions that improve surface conductivity. But selectivity of the material is a major concern as it can detect many gases. However, at higher temperature the detection is better. The challenge is to bring down the detection temperature without compromising with the selectivity. One of the ways to achieve the same is by the introduction of suitable dopants[66-71]. The addition of the foreign material decreases sensor operation temperature enhances sensitivity to different gases and increase in response and recovery time.

The conductivity change is appreciable on the surface of SnO_2 in the form of pellets, thick or thin films when a combustible gas is detected on the surface. Hence, change of conductivity is a surface phenomenon [72]. The negatively charged adsorbent is responsible for detecting gases such as H_2 and CO. The types of oxygen, which cover the surface of the oxide material, are O_2^-, O^- and O^{2-}. Yamazoe et al [73] reported that SnO_2 surface is covered by four kinds of oxygen which deabsorb around 80 ^oC (O_2), 150 ^oC (O_2^-) and 560 ^oC (O^- and O^{2-}). O^- is the most reactive of the lot with reactive gases in the temperature range 300-500 ^oC.

A number of techniques are used for synthesizing SnO_2 nanomaterials for gas sensing application. Some of the successful techniques are aerosol technique [74], condensation from vapor phase [75], solid–vapor process [76],

direct oxidation of tin at high temperature [77], hydrothermal treatment sol solution technique [78], hydrothermally treating α-stannic acid gel [79], laser-ablation technique [80], MOCVD technique using tetramethyltin and oxygen [81], wet chemical route [82], PECVD technique using dibutyltin diacetate as a precursor [83], sol–gel dip-coating technique [84-87], solvothermal treatment chemical process [88], thermal decomposition of Langmuir–Blodgett film precursors [89], thermal evaporation [90] and vapor–solid growth methods [91].

The different techniques give rise to different types of structures. Some of the established structures are nanobelts [76,92,93], nanocrystalline films [74,86,94], nanoparticles [78,79,81,84,88,95], nanopowder [96], nanoribbons [77], nanorods [83], nanoscaled thin films [74], , nanowires [75,80,90,97], thin films of nanocrystals and nanopores [98], ultrathin films [87,89], and wide variety of other nanoshapes [99].

Apart from the shape of SnO_2particles and their techniques of synthesis, there are other factors that affect the sensing properties. These include additives and thickness of the sensing material [78].

Vayssieres [99] showed the growth of wide variety of SnO_2 nanostructures on different substrates such as ITO, single crystal silicon and on glass substrates by thermodynamically controlled growth. Large scale deposition was carried out at low-temperature by aqueous thin-film growth technique. The SnO_2 nanorods and nanowires so formed predominantly grow along different crystal orientations. The SEM pictures explain the versatility of this technique to obtain different nanocrystalline forms of SnO_2sensing material. The surface area of these nanostructures can be exploited for gas sensing applications.

SnO_2 in the nanowire form can be efficiently employed for nano-electronic devices. Liu et al. [80] reported laser-ablation approach for large-scale synthesis of SnO_2 nanowires. Monodispersed gold clusters have been used to control the diameter of the nanowire. These nanowires can be used for FET devices which can be used in micro-gas sensors. The compatibility with silicon increases the possible applicability.

Kong and Li [77] reported the synthesis of CuO doped SnO_2 nanoribbons by direct oxidization of tin powders at about 810°C. The nanoribbons were successful in detecting 3-ppm H_2S gas at room temperature. A switch like behaviour for sensing was reported. The response time increased at elevated sensor operating temperature. However, the recovery time, for these devices, on the removal of H_2S is slow but improves with increasing temperature.

Huang et al. [83] have synthesized of SnO_2 nano-rods by PECVD technique for initial depositions and subsequent plasma treatments were used to modify the microstructure of them. Uniform 1-D SnO_2 nano-rods grown from the two-dimensional (2-D) films were observed in plasma-treated SnO_2 films. The optimal operating temperature of this plasma-treated SnO_2 thin film has decreased by 80°C and it increased the gas sensitivity by eightfold.

Xu et al. [100] explored the sensitivity of sintered ultrafine SnO_2 particles, in the range of 4–27 nm. The sensitivity for H_2 and CO was increased steeply when the average crystallite size was below 10 nm. The concentration value and operating temperature were 800 ppm and 300°C respectively for both the gases. Below 20 nm, sensitivity increases with

decreasing grain size, whereas below 10 nm this increase is found to be remarkable.

Rothschild and Komem[101] suggests that the gas-sensing mechanism of nanocrystalline metal oxides is unclear and the effect of grain size on the gas sensitivity, in the limit of nanosized grains, requires further clarification. Polycrystalline gas sensors pose the problem of grain coarsening during operation that causes an alteration of the gas response. Single crystalline nanobelts can be employed in gas sensors to overcome this problem. However, a high surface area to volume ratio is essential for a strong gas response as well.

Chen et al sensed ethanol. [102] Using SnO_2 nanorods synthesized through a hydrothermal route with extremely high sensitivity. The size distribution is 3–12 nm in diameter and lengths of 70–100 nm. This type of 1-D SnO_2 nanostructures is extensively applied to gas-sensing applications to detect NO_x, CO_x, H_2, C_2H_5OH, and H_2S gases. Such nanorods of SnO_2 are also reported without using any toxic organic chemicals during the synthesis [103].

Hydrothermal route was used by Baik et al [78] for synthesizing SnO_2 nanoparticles. The growth of the films is studied. The grains are observed to be stacked as revealed by FE-SEM. The average particle size is less than 10nm. The electrical resistance is found to be a function of temperature. A similar method is used and reaction between metal alkoxides and benzyl alcohol was explored to synthesize binary metal oxides. The synthesized particles were crystalline and have narrow size distribution. Niederberger et al. [88]were successful in synthesizing SnO_2nano-particles of size distribution

2-2.5 nm. The small size did not hamper the crystallinity and the distribution was observed to be perfect.

The growth of microstructured SnO_2 was assisted with the help of different metal layers which acted as seeds by Panchapakesan et al. [81]. The nanoparticle seeds have a decisive control over the growth of the structures. The variation of the seed produced different SnO_2 morphology.

Han et al [104] explored the control of crystallite size by doping SnO_2 with vanadium by co-precipitation method. The average crystallite size is observed to vary from 5.2 to 6.5 nm. The doping did not change the rutile structure, as the doping percentage was small. The crystallite size reduces with increase in doping.

SnO_2nano-particles, doped with ruthenium and rhodium impurities was reported by Pan et al [105]. Sol gel method with the aid of inorganic salt was used for the synthesis of the same. The nanoparticle size is 15nm. The as synthesized powder was annealed at 600 ^oC for further analysis. The sensing property of the sample was explored using petrol, C_4H_{10} and H_2 gases which showed that the sensing showed better results when the sample was doped with Ru. Petrol is detected between 200 ^oC and 300 ^oC and C_4H_{10} detected above 300 ^oC.

Cirera et al [106] synthesized doped and undoped SnO_2 powders for gas sensing with microwave assistance. The method is simple, fast and easy. Heat treatment was given to stabilize the synthesized sample. The palladium doping of the sample resulted in better sensing properties. The microwaved powders provide better electrical sensitivity towards CO and NO_2 gases. The results revealed low cross-sensitivity for the two gases.

Rare earth material samarium was used to dope SnO_2 by Wang et al [107] by hydrogen reduction method. The gases detected were 500ppm each of n-C_6H_{14}, H_2, C_2H_5OH, C_6H_6, and CO in air at 250°C. The sensitivity is found to depend on the oxygen vacancy.

Ag and Pt doped SnO_2 films were synthesized by Yu et al [108] by magnetron sputtering technique. Optical gas sensing was explored using the as-synthesized sample. The optical transmitivity gives a measure of the concentration value of alcohol in the atmosphere. It was observed that Ag doped SnO_2 is more sensitive to gas concentration below 10 vol%. For higher alcohol concentration Pt doped sample is a better agent.

7. CONCLUSION

The designing of the commercially viable gas sensor without compromising with the speed of response and selectivity is called for. The sophisticated synthesis method employed demands huge financial support and regular maintenance. Therefore, techniques like spray pyrolysis spin coating and dip coating is in existence from the 1950s and is one such system which can be designed and maintained at a very nominal cost. At the same time, thick and thin films can be deposited over a large area without losing uniformity. Tin oxide is one of the most prominent materials in the field of gas sensors. $SnCl_2.2H_2O$ is soluble in water and ethanol and hence is a good candidate for preparation of the precursor solution, which is used in spray pyrolysis. Pure SnO_2 has properties, which can be tailored easily by adding suitable dopants and/or varying the temperature conditions during synthesis procedure. This helps in even better detection of gases. The dopant can be

materials like the rare earth elements which substantially influences the conductivity mechanism. The porosity of the material helps in detection of gases utilising phenomenon of chemisorption or physisorption. The detection can be studied as an output signal in the form of changing electrical properties of the material when it meets the gas.

The electrical property of the as-deposited films can be explored experimentally using impedance analyzer with variation in temperature and frequency. The theoretical analysis of the same can be carried out employing software tools and difference algorithms. The electronic band structure and density of states (DOS) of the doped and the undoped sample can be explained using density functional theory approach.

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