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Research Paper

An Ethanol Sensor Review: Materials, Techniques and Performance

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Abstract

Sensing and detection of ethanol is essential for a various applications which include production of ethanol, fuel processing, chemical processing in industry, traffic management and societal applications. The advancement of nanotechnology has created huge potential to develop highly sensitive, portable, low cost sensors with low power consumption. A large number of materials and processes have been studied for the development of ethanol sensors. The large surface-to-volume ratio of nanostructures and nanomaterials is ideal for the adsorption of ethanol molecules. The advent of carbon nanotubes (CNTs) in particular, has advanced the development of gas sensors that exploit unique morphology, geometry, and material properties of CNTs. This review article focuses on the various methods and techniques used and various fabrication technologies involved in the development of ethanol sensors, and also reviews various performance characteristics of the sensors.

Keywords:- Ethanol sensors, selectivity, sensitivity, bismuth ferrite, redox reaction, thin films, nanostructures.

1 Introduction

Harmful gases are generated by industries and numerous other sources, rapidly deteriorates the environment; this leads not only to various health issues of humans, but also causes unnatural weather changes, environmental changes and ozone depletion[1].Hence, there is an urgent need for the detection of toxic and harmful gases. During the last few years, the demand for portable gas sensors has increased tremendously to detect the gases generated by industries, automobiles and environmental pollutants, etc. Therefore, there is a requirement for the development of efficient sensors having better sensitivity, selectivity, stability and a lower operating temperature.

Among the R & D efforts in the area of vapour sensors during the last few years, the work in the area of ethanol sensors has become extremely important. Ethanol vapour sensors with high selectivity and sensitivity have important applications as a device in traffic management, controlling the process of fermentation, food package testing for safety, wine making and medical applications. Ethanol is extensively used in liquors, scientific and industrial sectors.

The oxides of semiconductors such as ZnO, SnO_2[2 – 4], Fe_2O_3[5], $CuO - SnO_2$ [5], and others have been generally utilized as an economical sensor for hazardous, toxic and flammable vapours and gases in security and automotive applications.

The interesting physical properties of perovskite materials with the formula ABO_3 have generated enormous attention, and have found applications in several technological areas [6-8]. Among the perovskites, $BiFeO_3$ (BFO) is gaining prominence since it shows multiferroic properties simultaneously exhibits ferroelectric and ferromagnetic ordering [9-10].The sensor which is operating at room temperature is reported by Palkar et al.[11],who have demonstrated the performance of high resistivity thin films of $BiFeO_3$ as an ethanol sensor at room temperature. This paper reviews materials, methods and detection techniques for ethanol sensing, fabrication techniques such as growth of thin films, sensor development and evaluation of their performance measures such as sensitivity, selectivity, response and recovery time.

2 Materials for Ethanol Sensor

There are varieties of materials used for detection of ethanol in the last few years. Most important materials used are: ZnO, Al_2O_3, Multiwalled Carbon Nano Tube (MWCNT)-doped ZnO, Indium Zinc Oxide, polyaniline (PANi) with MWCNT, magnesium ferrite, $CdIn_2O_4$ nanoparticles, vanadium pentoxide, SnO_2, Sb doped SnO_2,TiO_2-doped SnO_2, mesoporous $ZnO - SnO_2$, titanium oxide, $LaFeO_3$, bismuth ferrite and barium substituted bismuth ferrite.

The ethanol gas detecting properties for thick flims of doped and pure zinc oxides were investigated by Patil et al. [5]. Screen printing techniques was utilized to prepare the thick films of pure ZnO. The effect of doping and microstructure of the film on the gas response, selectivity, response time and recovery time when exposed to ethanol vapours were studied and discussed. Pure ZnO

is practically insensitive to ethanol. They have observed that thick films of aluminium oxide (1 wt. %) doped zinc oxide was highly sensitive to ethanol vapours at 300°C against gases like LPG, NH_3, Cl_2,CO_2, and H_2. A very fast response and recovery to ethanol vapours was shown by this sensor. By mixing multiwalled carbon nanotubes and ZnO, ethanol gas sensitive materials were studied by Shan et al. [12]. Chemical Vapour Deposition technique was used to synthesize MWCNTs. Their results showed that the ethanol detecting properties of zinc oxide sensor significantly enhanced by doping with MWCNTs. They also analysed the selectivity of 0.1 wt. % MWCNTs-doped zinc oxide sensors for various gases. The results demonstrated an excellent selectivity to ethanol. In another experiment, thin films of optimized indium zinc oxide were deposited using an electron beam evaporation method at room temperature and were used as ethanol sensing elements by Shyju et al. [13]. They found that indium zinc oxide can be effectively used as an ethanol sensor. The optimized operating temperature for the indium zinc oxide film is 200°C. Their results showed that an ethanol sensor based on indium zinc oxide film has quick recovery time, high response and selectivity to ethanol vapour. Composite thin film of polyaniline (PANi) with multiwall carbon nanotubes based ethanol sensor have been prepared using a spin coating technique by Jaisutti et al. [14]. Chemical oxidative polymerization of aniline using ammonium persulfate in hydrochloric (HCl) medium was used to synthesize PANi.

Godbole et al. [15] studied the ethanol sensing properties of magnesium ferrite sensor by determining the response of the sensor as a function of working temperature. Comparison results of the magnesium ferrite sensor response to ethanol and methanol vapours showed that, the sensor is more selective and sensitive to ethanol vapour. Their study explored the possibility of developing a fast responding and stable, magnesium ferrite based ethanol vapour sensor. Nanoparticles of $CdIn_2O_4$ with crystallite sizes of around 10 nm were prepared by Cao et al. [16] using indium isopropoxide and cadmium acetate reaction in benzyl alcohol. The fabricated sensor exhibited fast response, and recovery times to ethanol vapour. Their results demonstrated that the sensors based on $CdIn_2O_4$ nanocrystals have better performance than that of tin oxide and indium oxide sensors, making this material interesting for sensor devices, as well as for various related electrochemical applications. A fast response/recovery time was shown by this sensor at a working temperature of 260°C. Vanadium oxide thin films grown by RF reactive sputtering from a vanadium pentoxide target in an Ar–O_2 atmosphere for ethanol sensing application was studied by Micocci et al. [17]. These films, studied at a working temperature between 280 and 300°C, have shown a high sensitivity and selectivity to ethanol as compared to CO, $CO_2, CH_4 and NH_3$ gases.

Mei et al. [18] have synthesized nanostructures of SnO_2 by a simple hydrothermal method. Excellent selectivity and response to ethanol was exhibited by SnO_2 nanostructures. The fabricated sensor can sense ethanol vapour as low as 50 ppb at a temperature of 285°C. Gas sensing characteristics of uncoated SnO_2 nanowires (NWs) were compared with those of SnO_2 NWs sensor coated with a functional La_2O_3 by Hieu et al. [19]. When an undoped SnO_2 NWs sensor was exposed to 100 ppm CH_3COCH_3 and C_2H_5OH, the responses measured as R_{air}/R_{gas}, (where, R_{air}: resistance in air, R_{gas}: resistance in gas) were 9.6 and 10.5, respectively, but those of CO, C_3H_8 and H_2 ranged from 3.1 to 3.3. The response values of SnO_2 NWs covered with La_2O_3 when exposed to 100 ppm CH_3COCH_3 and C_2H_5OH were 34.9 and 57.3, respectively, while CO, C_3H_8 and H_2 showed no significant change in their responses. Wu. [20] has studied the electrical and optical properties of SnO_2 nano wires which can be modulated by Sb-doping. P-type behaviour was exhibited by SnO_2: Sb nanowires. The tin oxide nanostructures have been used in gas sensors; but sensors that work at room temperature, including p-type SnO_2: Sb nanowires, have rarely been reported.

Zeng et al. [21] have synthesized thick film of titanium oxide-doped tin oxide nano powder using sol-gel method and fabricated the semiconductor ethanol sensor for which enhancement of sensitivity can be realized by exposing it to UV light. For ethanol vapour at room temperature, the $SnO_2 - TiO_2$ sensor exhibited high sensitivity and fast response/recovery time. The improved sensing properties make the $SnO_2 - TiO_2$ thick films promising as a detecting material for the new gas sensor application. The selectivity of TiO_2 nanoparticles for gases like C_2H_5OH, CH_4 and H_2 was investigated by Arafat et al. [22].By post heat- treating the samples at high temperatures in the range 750°C and 1000°C, the morphology and phase content of the particles was retained as characterized by X-ray Diffraction (XRD) analysis, transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM). For fabrication of the sensor, a TiO_2 film was printed on alumina substrate with gold interdigitated pattern. When the operating temperature of the sensor was varied in the range of 450°C to 650°C for varying concentrations of target gases, the sensor showed an ultra-high response to ethanol vapour compared to H_2 and CH_4. The maximum detecting temperature of the sensor was found to be 600°C. For an ethanol concentration of 20 ppm at the optimum sensing temperature, the recovery and response times of the sensor were found to be 3 min and 15 min, respectively. It is proposed that the ultra-high response of the sensor is because of the catalytic action of TiO_2 with ethanol.

A high sensitive mesoporous $ZnO - SnO_2$ nanofibers-based ethanol sensor was fabricated by Song et al. [23]. With the sensitization of evenly distributed mesopores and heterostructure of zinc oxide and tin oxide, the fabricated sensor showed good sensing properties for ethanol such as high sensitivity, quick response, reproducibility and linearity. The sensitivity increased with the increase in concentration of ethanol. This mesoporous zinc oxide–tin oxide nanofibers are very favourable materials for ethanol sensors.

Hossein-Babaei et al. [24] have developed titanium oxide thin film deposited on thermally oxidized Si wafers by sol–gel technique, which was subsequently heat-treated at 500°C in air. Nano-crystalline thin-film of $LaFeO_3$ perovskite-type composite-oxides were achieved by Zhao et al. [25] using a sol–gel coating method. To etch and pattern the thin film, photo-etching method was used. The authors reported that the sensor has exceptional selectivity, good stability and a good sensitivity to ethanol. The authors also investigated $LaFeO_3$ doped with strontium ions to improve the sensor recovery time.

A highly resistive bismuth ferrite thin film was synthesized by Patel et al. [26].The thin films of BFO were grown on different substrates including Si, SiO_2, platinized silicon and quartz; the deposition conditions were varied so as to get the preferred oxygen stoichiometry in the films by pulsed laser deposition technique at different oxygen pressures. XRD measurement showed the pure phase of the film. The film deposited was highly resistive. The room temperature resistivity measurement on exposure of ethanol was carried out in order to determine ethanol sensing property. Pure and barium substituted bismuth ferrite samples were prepared by Dong et al. [27] via sol–gel method. They compared the conduction and gas sensing properties of barium substituted bismuth ferrite with pure bismuth ferrite and found that the conduction of $Bi_{0.9}Ba_{0.1}FeO_{2.95}$ (BBFO10) is overwhelmed by p-type hole conduction. The upgraded gas-detecting characteristics of the BBFO10 sensor are attributed to the higher oxygen vacancy concentration which was produced by adding of Bi^{3+} ion by an aliovalent Ba^{2+} ion at the A-site of the perovskite structure.

3 Methods and Techniques

3.1 Basic Principle

The thin films of metal oxides are considered as promising choices for ethanol vapour sensors. Chemical and physical characteristics of the metal oxides, the measurement condition, their synthesis techniques and nature of gases mainly determine the sensor properties [28]. Chemiresistance is the basic principle behind the working of metal oxide gas sensors viz.the electrical resistivity or conductivity of thin films changes when they are exposed to a target gas. In other words, the resistivity of the metal oxide is modified by gas molecules which either act as an acceptor or donor of charge carriers while interacting with the metal oxides. The decrease or increase of resistance of the metal oxide thin films are due to the nature of the gas molecules in surrounding air and type of majority carriers in the semiconductor thin film. For n-type materials, oxidizing gases increase the resistance of thin films, whereas for p-type materials, reducing gases decrease the resistance. The receptor function (REDOX) along with the transduction function describes the chemiresistive behaviour of the metal oxide gas sensor. The sensors based on metal oxides can be in the form of thick or thin films or in the form of sintered pellets. In particular, the receptor and transduction functions are decided by the crystallites structure of the materials and the interconnectivity between crystallites.

A redox reaction is a chemical reaction; it includes a transfer of at least one electron from one molecule to another. Substances that are capable of removing an electron are said to be oxidative and are called as oxidizers. The oxidizer is reduced when oxidant accepts electron from another substance. Substances that are capable of transferring electron are said to be reductants and are called reducers. Reductant is oxidised, when reductant donate electron to the other substance.

Ethanol is being used in industries and in many laboratories for various applications and hence, it is one of the very important organic molecules to be identified in the environment. Functional group of the absorbed ethanol dissociates as water vapour or hydrogen molecule based on whether the metal oxide surface is basic or acidic. Dissociation into hydrogen molecule (dehydrogenation) or water vapour (dehydration) process leads to desorption of water vapour and CO_2 gas molecule via the formation of acetaldehyde (CH_3CHO) and cyclobutadiene (C_2H_4).The desorption of ethanol is considered by the partial pressure of oxygen in the ambient. Cyclic process of ethanol absorption reduces the content of oxygen in the atmosphere, thus the intermediate products react with the lattice oxygen in the metal oxide surface, and result in the creation of oxygen vacancies in the lattice. Due to REDOX process the concentration of electron in metal oxide surface is increased by oxygen desorption from the lattice and surface. However, the desorption of carbon dioxide from the surface was discovered from the in-situ gas chromatography investigation of ethanol reaction with metal oxide material. The basic or acidic nature of the surface can be modified by the absorption of separated hydrogen and hydroxyl ions on the oxygen absorbed surface of the metal oxide.

3.2 Resistivity based detection

Resistivity based gas sensors were proposed fifty years ago for the first time. Toward the start of the 1960s, Seiyama was able to demonstrate that, utilizing ZnO thin film as a detecting layer, gas detection is possible with basic electrical devices [29]. Resistive gas sensors are electronic devices; electrical resistance of this sensor is a function of the surrounding gas ambient. Thus, resistive gas sensors are particularly suitable to detect different ambient gases and variation of their concentration [30]. However, their sensitivity and selectivity is limited, and hence, these deficiencies serve as a main driving force to develop new materials and methods for superior gas detection. Resistive gas sensors comprise a porous semiconductor layer, such as SnO_2, WO_3, TiO_2, ZnO, etc., which have sensitivity at elevated temperature, up to a few hundred degrees Celsius. This means that the sensors can be used to analyse even exhaust gases, but require additional energy for heating. Therefore, it is essential to introduce new methods, which can enhance the advances in gas sensing technology.

In resistive sensor the target gas impact on the total electronic resistance of the detecting material is a complex one. As per a standard model, an electron depletion layer thickness at the surface is changed by surface-chemical reaction of the gas molecule. It also affects the overall conductivity. Therefore, semiconductor interior regions do not contribute much to the response of the sensor; that is the reason tiny particles or, particularly, ordered mesoporous materials with thin pore walls offer the benefit of comparatively high sensitivity. These days, detailed methods are available to increase the selectivity of resistive sensors about specific gases, such as temperature-cycling within the sensitive layer or variation of measurement voltage for generating multiple signals out of a single layer [31].Synthesis of highly resistive bismuth ferrite thin film gas sensors based on the resistance change of the semiconductor in air effected by a reducing gas was reported by Patel et al. [26]. The resistivity of the film was measured using four probe measurement system. The p-type gas sensing properties in thin films of undoped titanium oxide have been reported by Hossein-Babaei et al. [24].They have used resistivity based detection to sense the ethanol gas. Wang et al. [32] have constructed an ethanol gas sensor by coating ZnO porous-shell hollow spheres on a ceramic tube having pre-fabricated measuring electrodes and heating coil. Resistive gas sensors are the most widely recognized kind of gas sensors because of the simple and robust function and minimal effort for fabrication.

3.3 FET based detection

An FET-based gas sensor consists of at least one field-effect transistor, one gas-sensitive layer and a reference layer. The field-effect structures are triggered by any changes in work function that occurs when materials of the layers are exposed to a gas. The gas-sensitive layer includes a metal oxide having an oxidation catalyst on its surface and is accessible to the measured gas. In an FET-based gas sensor the gate surface of the sensor is exposed to a chemically variable environment in which the gases to be measured exist. The FET having a solid electrolyte as gate material is only possible as a thin-film microdevice. The MOSFET gas sensor is a metal-insulator semiconductor device, in which the gate material interacts with some gases; due to variations in the work functions of the metal and the oxide layers, the threshold voltage of the sensor changes. The threshold voltage change is proportional to the analyte concentration. Also changes in the work function affects the of drain to source current and the gate voltage which can be utilized as the sensor output response. The heating element is not required for FET gas sensor because of its very high input impedance and hence, can work at room temperature. It can be utilized in small detecting arrays on one single chip and its detecting materials do not need to be a semiconductor; different materials like metallic conductors can also be utilised [33].

An ethanol-sensitive FET, by using a $LaFeO_3$ nano-crystalline thin-film as a gate electrode of an ordinary n-channel MOSFET, has been developed by Zhao et al. [25]. They have combined thin-film technology with the NMOS integrated circuit technology. The conductance of single-walled semiconducting carbon nanotubes in FET geometry was measured by Someya et al. [34]. They have investigated the response of the device to ethanol vapours and huge variation in drain current of FET was observed, when the device is exposed to different levels of ethanol vapours. These responses are reproducible and reversible for several cycles of ethanol vapour exposure. Their analyses show that carbon nanotube FETs are sensitive to various levels of ethanol vapours.

Another method is back-gated graphene FET array on micro channels examined by Chen et al.[35].Their work gives an improved method for building back-gated graphene FETs for ethanol detection applications.

3.4 Capacitive based detection

In a capacitive sensor, permittivity change of a dielectric is considered relying upon the target gas concentration. The impedance spectroscopic methods are generally applied for this technique in a lab environment. The sensor-active material is subjected to an alternating voltage source, whose frequency is varied over time to determine the permittivity. The permittivity can be calculated by recording the current and phase relationships. By considering only physisorption impacts and neglecting nonreversible chemical reactions of the target gases with the detecting material, this method is appropriate for gases having high permittivity values, such as NH_3 or water vapour, but not so much for, e.g., CH_4. Consequently, humidity detection is the primary use of mesoporous materials inside capacitive sensing field. Since physisorption of the target gases assumes an imperative part in this idea, the advantages from utilizing well-ordered mesoporous materials having even pore sizes and defined absorption properties are self-evident. Along with physisorption, proton conductivity at the surface with a porous silica material was likewise appeared to influence the sensor's response because of partial short-circuiting inside the detecting layer. In this study, the impact of surface OH groups in mesoporous silica films was investigated. The hydrophobisation, which is likely to suppress proton conductivity, was found to bring about a strong reduction in sensitivity, because of poor physisorption characteristics of water [31].

Characterization of silicon nanoporous pillar array which is used as capacitive ethanol sensor at room-temperature was studied by Li et al.[36]. With concentration of ethanol varying from 0 to 500 ppm, an increase in capacitance over 430% was accomplished at a signal frequency of 200 Hz. The response of the device was found to be dependent on concentration, low at lower concentration and high at higher concentration.

4 Growth of thin films and measurement technique

4.1 Growth of thin films of sensor material

The thin film is a layer of material whose thickness varies from a couple of nanometers to a few micrometers. A procedure for growing a thin film of material on the surface of a substrate is called thin-film deposition. The property of the thin film mainly relies on grain size, crystallinity and surface morphology. Hence, a thin film growth technique assumes an important part in sensor properties of the material. Therefore, appropriate thin film growth techniques and fabrication procedures have to be adopted for the development of very efficient alcohol sensor device. There are many thin film deposition techniques available. The major techniques used are chemical solution deposition, spin coating, pulsed laser deposition, chemical vapour deposition, spray pyrolysis and sputtering.

In chemical solution deposition (CSD) technique a liquid precursor is utilized which is normally a solution of organometallic powders dissolved in an organic solvent. The CSD is otherwise called as sol-gel technique on the grounds that 'sol' gradually evolves resulting in the development of a gel-like diphasic system. In this small molecules are utilized to produce solid materials. The technique is utilized for the manufacturing of metal oxides, particularly silicon oxide and titanium oxide. The procedure includes conversion of monomers into a colloidal solution which acts as the precursor for an integrated network of either discrete particles or network polymers. Metal alkoxides are the typical precursors. The precursor medium, stabilizing agent, ratio of solute and stabilizing agent, time required for processing, temperature required for drying, preheating temperature, dip coating ,ratio of dip to retrieval speed and dip duration are important parameters. Further, number of dip spin coating and speed of substrate rotation and number of cycles are the optimizing parameters for thin film depositions. Zhao et al. obtained nano-crystalline thin-film containing perovskite-type composite oxides of $LaFeO_3$ by utilizing a sol–gel coating method [25]. The sol-gel method which is utilised to grow layers of titanium oxide on thermally oxidized Si wafers was studied by Hossein-babaei et al. [24].Chemical solution deposition is a relatively cheap, simple thin film deposition technique that is capable to create stoichiometrically exact crystalline phases.

The spin coating or spin casting is a technique which is utilised to deposit thin films on a flat substrates. The solution spin speed and solution viscosity determines ultimate thickness of the deposited film. To increase the deposition thickness of the films as desired, depositions can be carried out on a repeated basis. The thermal treatment is usually carried out to crystallize the amorphous spin coated film. The crystalline films can show some orientations after crystallization on single crystal substrates. The applied solvent is generally volatile, and evaporates simultaneously. The viscosity, angular speed of spinning, and concentration of the solution and the solvent determines the thickness of the film. Thinner films are obtained for higher angular speed of spinning.

In the process of spray pyrolysis, deposition of thin film is carried out by spraying a solution on a heated surface, on which the components react to form a thin film. The thin films obtained by spray pyrolysis are utilized for different devices such as sensors, solar cells, and solid oxide fuel cells. Optimizing key parameters of this process are substrate temperature, spray nozzle/gun diameter, substrate-spray nozzle distance, applied gas pressure and flow rate of the solution.

Sputtering is an important process in which target material is bombarded with energetic particles like gas ions, resulting in ejection of particles from the target; it is normally used for deposition of thin-films, etching and analytical techniques. Sputtering is carried out either utilizing DC Voltage (DC Sputtering) or utilizing AC Voltage (RF Sputtering). In DC Sputtering, voltage is set in the range of 3-5 KV and in case of RF Sputtering; the power supply is set at a frequency of 13.56 MHz. The optimizing key parameters of this process are source to substrate distance, anode potential, temperature of the substrate, ratio of argon and other (oxygen) gas, deposition time, working pressure and RF applied power. Thin films of oxides are prepared using reactive sputtering process in an $Ar - O_2$ mixer[17].

Pulsed laser deposition (PLD) is a method, in which a pulsed high power beam is focused inside a vacuum chamber so as to strike a target of the material which is to be deposited. This material is ablated from the target which is deposited as thin film on a substrate. The process is carried out in ultra-high vacuum or in a background gas, such as oxygen that is normally utilized while growing oxides to completely oxygenate the deposited films. Absorption of laser pulse at target causes electronic excitation followed by thermal excitation leading to ablation, plasma formation and even exfoliation. The species which are ejected in the form of a plume consisting of several energetic species including atoms, molecules, electrons, clusters, ions, particulates and molten globules, and deposit on a hot substrate. The BFO thin films were deposited by Patel et al. [26] on different substrates like Si, SiO_2, Pt/Si, Quartz using pulsed laser deposition technique with KrF-excimer laser having wavelength of 248 nm under oxygen pressure in the range of 0.5-0.05 mbar, substrate temperature in the range 600-750°C and with laser fluence 2 J/cm^2.

Considering all the above thin film growth techniques, PLD is the preferred technique for growth of thin films of oxides and insulators because it reproduces cationic stoichiometry in the film.

4.2 Ethanol sensor measurement technique

As mentioned earlier, redox reaction is the basic principle for ethanol sensing mechanism. This occurs mainly on the surface, hence surface morphology of films and nanostructures play vital role both in determining sensitivity and selectivity of ethanol sensors. After the growth of thin films with optimised surface morphology, efficient fabrication techniques have to be followed for the development of an ethanol sensor device.

A typical ethanol sensing scheme based on surface sensitive interdigitated pattern is shown in Figure 1. The interdigitated pattern of Cr/Au film evaporated on the sensor film using shadow mask enables the detection of changes in surface resistance of the sensing film when it is exposed to ethanol vapours. Figure 2 shows schematic of ethanol sensor measurement setup with an input gas inlet and vacuum port for evacuation. The ethanol vapours will be carried by nitrogen gas into the measurement setup, which will expose the sensor material. A dilution system can be used to vary the concentration of ethanol input in the measurement setup. The resistance of the ethanol sensor thin films with interdigitated pattern is measured using a source meter. Both frequency dependent capacitance and impedance values can be used to analyse sensor response to ethanol. Sensor response can be examined across the wide range of vapour saturation and the detection limit for ethanol. The response and recovery times of ethanol sensor can be determined from the response curves. Further, sensor performance can be examined with time to find out aging effect.

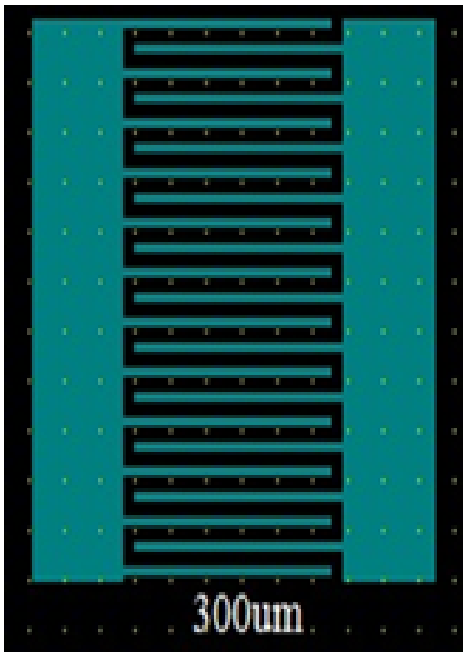

Figure 1: Sensing scheme - interdigitated metal contacts for measurement of resistance of sensor device.

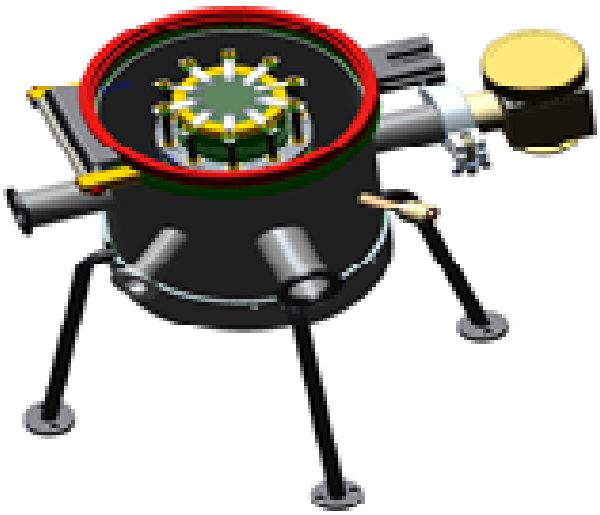

Figure 2: Schematic of ethanol sensor measurement setup with vacuum port for evacuation, sample holder and manual probes.

5 Performance of alcohol sensors

Sensitivity, selectivity, response and recovery time are typically reported as the main performance parameters of ethanol sensor. Table 1 shows performance parameters of ethanol sensors based on various materials.

Sensitivity of a sensor is obtained by comparing parameters of the device such as conductance, resistance, current, threshold voltage and mobility etc., before and after exposure of target gas. Sensitivity S is characterized as R_{air}/R_{gas}(where R_{air} is the resistance in surrounding air and R_{gas} is the resistance of the device when presented to target gas).Selectivity is used to measure the property of a sensor to react specifically to a target gas. The response time (recovery time) is normally determined as the time period required for the device to experience 10% change to 90% change (or from 90% change to 10% change) in the value of the test signal at equilibrium after exposing to a target gas.

Table 1: Performance Parameters of Chemiresistive Based Ethanol Sensors.

Materials	Sensitivity for C_2H_5OH	Poor selectivity for	Response time	Recovery time	Operating temperature
p-type barium-substituted bismuth ferrite[27]	∼5 (for 100 ppm)	Toluene, Methanol, Gasoline, Acetone, Ammonia, Formaldehyde.	∼3 sec	∼10 sec	400°C
MWNTs/ ZnO [12]	46 (for 50 ppm)	Different gases	4 sec	20 sec	260°C
Vanadium oxide thin film [17]	∼2(for ∼15 ppm)	CO, CO_2, CH_4, NH_3	∼16 min	∼20 min	300°C
$LaNiO_3$ [40]	20 (for 200 ppm)	CO_2, H_2O	∼5 sec	NA*	400°C
0–1 weight % In-doped SnO_2,	110 (for 1000 ppm 0.5 wt. % In/SnO_2)	H_2S, CH_4	2 sec	2-3 min	300°C
0.1–5 weight % GP/In- doped SnO_2 [37]	965 (for 1000 ppm 0.5 wt. % In/SnO_2/5 wt. % G)	H_2S, CH_4	1.8 sec	1-2 min	350°C
ZnO Nanorods [41]	29.7 (for 100 ppm)	H_2, NH_3	NA*	NA*	300°C
ZnO–SnO_2 nanofiber [23]	18 (for 100 ppm)	NO_2, NO, NH_3, C_2H_2, CH_4, H_2, CO_2	5 sec	6 sec	300°C
SnO_2-reduced graphene oxide (SnO_2-rGO) [42]	22 (for 1.12 ppm)	H_2S	5 sec	9 sec	300°C
SnO_2 Doped Poly-Diallyldimethylammonium Chloride [43]	71.6 (for 150 ppm)	NO_2, H_2, SO_2, H_2S	88 sec	NA*	RT**

Nano Fe_2O_3 [44]	180(for 250 ppm)	CO, CO_2, NH_3, LPG, H_2, Cl_2, H_2S	7 sec	32 sec	350°C
α-Fe_2O_3/ SnO_2 core-shell nanorods [45]	19.6 (for 10 ppm)	NA*	<30 sec	<30 sec	220°C
In_2O_3 nanowires [46]	∼2 (for 100 ppm)	CH_4, CH_3OH	10 sec	∼20 sec	370°C
ZnO nanorods [48]	∼10(for 1 ppm)	H_2, CO, N_2 and CO_2	NA*	NA*	300°C
ZnO nanorods [49]	∼20(for 100 ppm)	NA*	10 sec	5 sec	∼325°C
SnO_2 1 wt% Ag/SnO_2, Ag@ SnO_2 [38]	1.48(for 200 ppm), 1.24, 2.24	NA*	55 sec 52 sec 34 sec	85 sec 53 sec 68 sec	RT**
Hexagonal indium oxide nanorods (H-In_2O_3) [47]	11.5(for 50 ppm)	90# gasoline, 97# gasoline, CH_4, Benzene, Toluene, LPG and ammonia	6 sec	11 sec	330°C
TiO_2 Nanoparticles [22]	∼2.5 $\times 10^5$ (for 20 ppm)	H_2 and CH_4	3 min	15 min	600°C
Aloe-like SnO_2 [18]	23(for 50 ppm)	Methanol, Acetone, Isopropanol and Ammonia	1.2 sec	76 sec	285°C
Zinc oxide porous-shell hollow spheres [32]	∼80 (for 300 ppm)	Methanol, Formaldehyde and Benzene.	∼5–12 sec	∼ 8-13 sec	350°C
Silicon nanoporous pillar array (Si-NPA)*** [36]	7% (for 50ppm)	NA*	15 sec	30 sec	RT**
SnO_2:Sb nano wires**** [20]	1.13 (for 40 ppm)	NA*	∼9 sec	∼44 sec	RT**
Back-gated graphene FET**** [35]	17%	NA*	NA*	NA*	NA*

*Not Available,**Room Temperature,***Capacitive based, ****FET based

6 Summary

In this paper, we have reviewed ethanol sensing materials and technologies. A classification of ethanol sensor performance based on sensing materials, their surface structure and variation of electrical resistance has been presented. Ethanol sensors, by and large have been found to be extremely surface-sensitive mainly because the primary reaction is chemi-resistive which occurs on the surface exposed to ethanol. Considering two key performance parameters-sensitivity and selectivity, various kinds of sensing materials and technologies are compared and evaluated. A typical experimental setup for chemi-resistive based measurement has been presented.

It is expected that with advances in materials and technologies, ethanol sensors with high sensitivity as well as reliability, which have important application potential as a device in traffic management, food ferment, wine making and medical processes would be developed.

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