Nanostructured Metal Oxide Based Thick Film Sensors

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Abstract **-Sensors form a vital part of any measurement and control system. Currently available gas sensors detect gases at high temperatures, i.e. > 100°C. In the present work, efforts have been made towards developing sensors which provide higher sensitivity, comparatively low operating temperature and improved long-term stability at reduced cost. This is possible with the hybrid Thick Film Technology (TFT) which offers flexibility in the choice of materials and design, easy integration with electronic circuits and packaging. We have done a survey of different base materials, i.e. SnO_2, TiO_2 and ZnO for construction of these sensors. Out of which we have chosen SnO_2 and TiO_2 as basic sensing material. We have done the detection of different gases such as hydrogen, ethanol, and ammonia for detection purpose. The aim was to develop gas sensors which will detect gases at lower temperatures (<100°C). We have successfully done so using TiO_2 and SnO_2 sensors, but we have obtained better results using TiO_2 i.e. gas detection in the range of 50 to 70 °C. In recent years, nanomaterials have been widely studied as potential candidates for the fabrication of gas sensors as they provide higher surface-to-volume ratio. The use of semiconductor oxide sensor fabrication is the preferred manufacturing process due to its better performance and potentially low cost.**

Keywords- **Nanomaterials, parts per million (ppm), Thick film technology, Tin dioxide, Titanium dioxide.**

I. INTRODUCTION

A sensor is an energy converter; it converts any type of energy to electrical.

There are two main types of sensors: active and passive.

An active sensor is the one which may not need an additional energy source to generate electrical signal as a response of sensory interaction with the stimulus. Eg. Thermocouple, piezoelectric sensor, etc.

Passive sensor requires an external power source to operate.

II. NEED FOR GAS SENSORS

Detection of pollutant, toxic, refining, combustible and process gases is important for system and process control, safety monitoring and environmental protection.

Gas sensors based on solid state semiconductor materials offer considerable advantages compared to other gas sensing methods.

Semiconductor sensors are inexpensive to produce, easy to miniaturize, rugged, reliable and can be designed to operate over a range of conditions like high temperatures. [1] Sensors find applications in aerospace, laboratories, factories, fuel cells etc.

The properties of metal oxides have received a great deal of interest for many years, due to applications in various fields such as solar cells, optical devices and oxidation catalysts. Numerous metal oxide semiconductor materials have been reported to be usable as gas sensors, such as Zinc oxide (ZnO), Tin dioxide (SnO_2), and Titanium dioxide (TiO_2). These materials have non-stoichiometric structure, so free electron, originating from oxygen vacancies contribute to electrical conductivity.SnO_2 is extensively studied because of its interest in both the application and the fundamental research in the last decade due to its remarkable optical and electrical properties.

TFT proved as an alternative to the conventional sensor assembly. Sensors realized in thick film technology are normally exposed to harsh environmental conditions. Besides thick film technology provides a cost efficient production of sensors.

Nanostructured materials are of great interest nowadays because of their small size, which gives a large surface area; they can lead to dramatically differing properties than the bulk.

Synthesis and investigation of nanoscale materials along with tuning the overall properties of these particles to fit targeted applications are at present, among the most active research areas.

In 1970, Figaro Engineering Inc. fabricated and commercialized the first metal oxide gas sensor device; since then, a large variety of gas sensors have been developed (electrochemical, catalytic combustion, etc.), but, up to the present, their market is still very low, less than 2% of the whole sensor market including lambda sensors. The demand of gas sensors, both for outdoor and indoor applications (measurement of pollutant gases in atmosphere, gas emission control, air quality assessment in houses, in cars or in work places, gas sensors for safety, for example hydrogen sensors in fire alarms, and so on) is continuously increasing.

Thick film technology offers advantages of low cost, production amenability and automation. It's used in hybrid circuit technology, where it offers the added advantages of reliability and miniaturization, is well known. It is a flexible and versatile technology wherein resistors and capacitors of various values can be printed and obtained after firing.

III. NANOSTRUCTURE MATERIALS

Nano-science deals with materials having structures in nano-meter scales. Typically, these materials are characterized by dimensions (1nm= 10^{-9}m). Nano-science explores the nature of matters between atoms and molecules (defined by quantum mechanics) and condensed matters (defined by solid state chemistry/physics). [1][2]

Because of their small size, which gives a large surface area, they can lead to unexpected or dramatically differing properties than the bulk. They are useful candidates for many applications like optoelectronic devices, catalysis, display devices, photo and electroluminescent devices, spintronics, sensors etc.

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IV. TiO_2 SENSOR

Titanium dioxide thin films are extensively studied for applications in solid state gas sensor devices. Their gas sensing properties are strongly dependent on deposition technique, annealing temperature,film thickness and consequent properties like crystalline structure, grain size or amount of defects and impurities.

Titanium dioxide (TiO_2) is an important multifunctional material being used as photo-catalyst in solar cells, for the production of hydrogen, as a corrosion-protective coating, as an optical coating, as a gate insulator in MOSFETs, etc. In recent years a large number of contributions have reported the extraordinary sensitivity of TiO_2 towards H_2. TiO_2 also shows good sensing properties to CO, ethanol, CH_4, etc. and have an advantage of being chemically stable at high temperatures which makes it a good candidate for gas sensing applications.

However, the main disadvantage of these gas sensors is the inability to distinguish between gases, but it has been reported that the selectivity could be improved by dopants.

The working principle of Semiconductor Metal Oxide (SMO) gas sensors is based on the change of their resistivity upon exposure to specific gas.

V. FIRING PROCESS FOR A PASTE

This section we will explain the firing profiles used for fabrication of sensors. After the paste is screened on the substrate, it allows to level for 15 minutes at room temperature. Firing is then undertaken at temperature between 500- 1000°C. The typical firing profile for an air is illustrated in the figure below

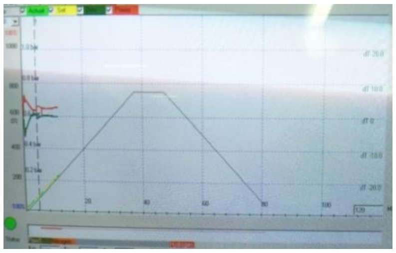

Fig. 1 Sensor film firing profile

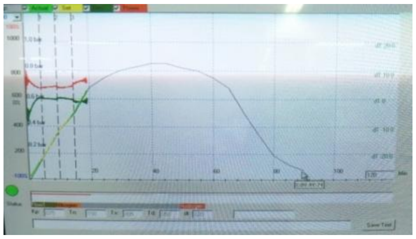

Fig. 2 Electrode firing profile

The firing of the film determined by the complete reaction of the system and determines the final resistivity of films.

The resistive material in comparison to conductors is normally very sensitive to firing conduction and require very precise control over temperature and firing time. During the firing process, a number of important reactions (both chemical and physical) occurred and finally the mechanical and electrical properties of thick films are developed.

3.1 The brief description of these reactions is given below:

Thick-film technology consists of these sequential screen printing and firing of layers of various materials onto an insulating substrate. Thick film printing involves, in general, a mechanical squeegee which is part of a standard thick film screen printing machine. As the term screen-printing suggests, this printing process uses a screen in which the pattern of the printed design is placed. One of important features in the thick film printing is the components of the paste which is a material used to form the printed layer, and the function of the layer is directly derived from the components of the paste: the active material of interest, a binder and a solvent. A typical thick film screen consists of a finely woven mesh of nylon, mounted under tension on a wooden or metal frame. The mesh is coated with an ultra-violet (UV) sensitive emulsion onto which the pattern of the device can be formed photolithographically.

The finished stencil has an open mesh area through which the desired pattern can be printed.

Fig. 3 Screen with printing pattern

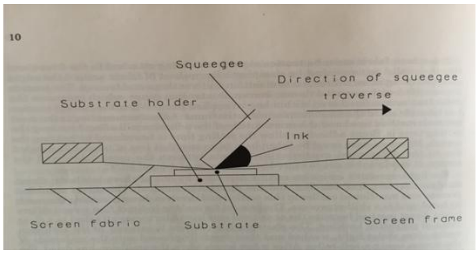

Fig. 4 The basic screen printing process [4]

The paste is placed on the opposite side of the screen and a squeegee traverses the screen under pressure, thereby bringing it into contact with the substrate and also forcing the ink/paste through the open area of the mesh. The required pattern of the device is thus left on the substrate. The next stage is to dry the film to remove the organic solvents from the paste. After this stage, the dried film is relatively mechanically stable and the film sample can be handled. All thick film pastes contain glass, and during the firing cycle the glass melts and forms a mechanical key at the film-to-substrate interface, and also provides a suitable matrix for the active material of the film. The result is a fired composite film that is firmly bonded to the substrate.[3]

VI. SPECIFICATIONS OF SENSORS

In this section, we will be defining different sensor specifications like gas response and aging.

The important specifications of the sensors are:

(a) Response
(b) Sensitivity
(c) Working range
(d) Accuracy
(e) Aging

Sensor specification like stability, response and recovery time, linearity are the most essential features of sensors. The sensor response is usually defined as

$Rs = \frac{Rair}{Rgas}$ Rair < Rgas .... (3.1)

$Rs = \frac{Rgas}{Rair}$ Rgas > Rair ....(3.2)

Where Rs is the sensor response or sensitivity of the gas sensor.

(Rair and Rgas are electrical signal values at equilibrium in the presence of gas and in reference gas, respectively). Depending on reducing or oxidizing gas of the chemical species interacting with the sensor surface the equation will be used. The reducing gases (H_2, NH_3,C_2H_5OH, LPG, etc.) will cause a decrease in electronic resistance of the samples compared to the resistance in the air. The equation is the normalization of output to input (change in resistance of the sensor in the presence of air + test gas divided by the initial resistance of that sample in only air). The different definitions of response are used in literature for studying of gas sensing performance of the materials.

VII. RESULTS

A. *Scanning Electron Microscopy (SEM)*

This section explains the morphology of TiO_2 particles and whether there are any defects present in the sensor material. SEM depicts the microstructure of the sensor.

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons.

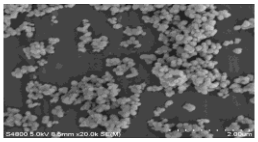

Fig. 5 SEM of TiO_2

B. *X Ray Diffraction*

Presence of peaks in this XRD image denotes the presence of defects and doping. Since there are no peaks observed, we conclude that the TiO_2 sensor is defect free and is not doped.

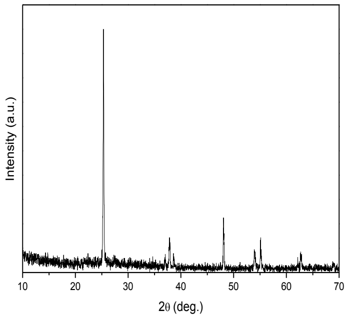

Fig. 6 XRD of TiO_2

C. *TiO_2 GAS SENSOR*

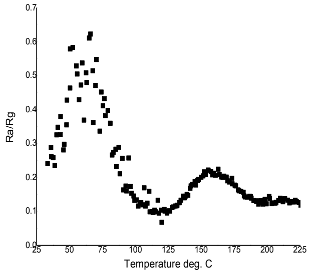

Fig. 7 TiO_2 sensing for ethanol gas 160 ppm

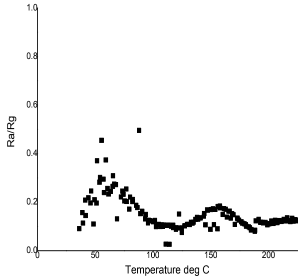

Fig. 8 TiO_2 sensing for ethanol gas 320 ppm

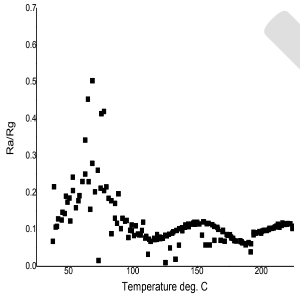

Fig. 9 TiO_2 sensing for ethanol gas 480 ppm

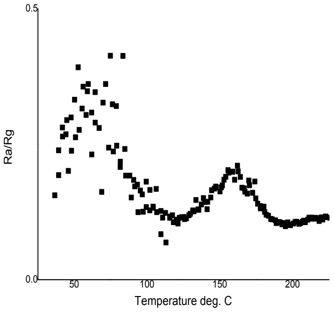

Fig. 10 TiO_2 sensing for hydrogen gas 160 ppm

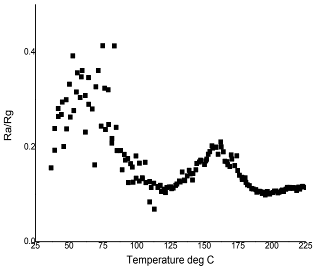

Fig. 11 TiO_2 sensing for hydrogen gas 320 ppm

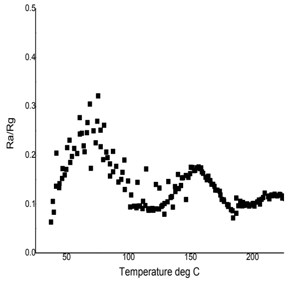

Fig. 12 TiO_2 sensing for hydrogen gas 480 ppm

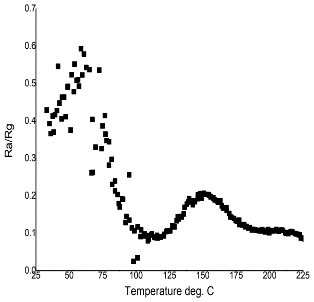

Fig. 13 TiO_2 sensing for ammonia gas 160 ppm

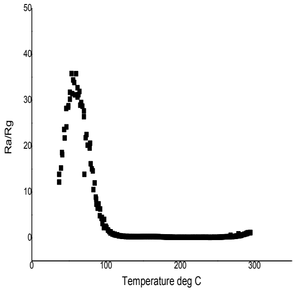

Fig. 14 TiO_2 sensing for ammonia gas 320 ppm

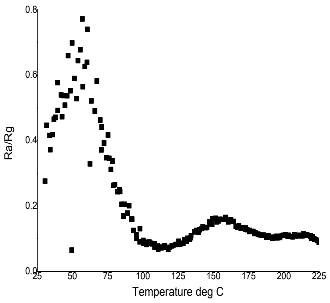

Fig. 15 TiO_2 sensing for ammonia gas 480 ppm

The following table shows the TiO_2 sensor response to different gases.

Table I.

TiO_2 Sensor response

Gas	Operating temp. (°C)	Response Ra/Rg
Ammonia		
160 ppm	66.0	0.55
320 ppm	55.0	33.9
480 ppm	68.0	0.7
Ethanol		
160 ppm	62.0	0.5
320 ppm	60.0	0.3
480 ppm	58.0	0.7
Hydrogen		
160 ppm	57.0	0.3
320 ppm	66.0	0.3
480 ppm	75.0	0.26

VIII. CONCLUSION

We have prepared nano size TiO_2 based thick film based gas sensor for sensing of different gases. The particle size of the material is around 50-150 nm. The sensor showed very good response to Ammonia gas of 320 parts per million (ppm) at the operating temperature of 61°C.

Resistive type sensors have been successfully fabricated and studied in this work. The structural, microstructural analysis revealed the nano size of these sensors. [5] [6] A comparative study of the hydrogen, ethanol and ammonia sensing properties viz. operating temperature, sensitivity and aging of thick film TiO_2 sensors was carried out. Experimental results have shown that TiO_2 sensors are sensitive to low gas concentrations.

IX. FUTURE SCOPE

Thick film sensors have tremendous scope for improvement in the future. The development of thick film semiconductor gas sensors is likely to progress in 3 broad fashions.

Sensors for both oxygen and impurities in the air will benefit from evolutionary improvements in manufacturing quality.

A second route forward is through the use of alternative materials the perovskite structure varieties that offer temperature alternative to titanium dioxide have been mentioned. This trend is likely to continue as the necessary chemical and micro structural control is developed for each preferred composition.

The third direction of future development will be towards the use of more sophisticated design concepts. The fundamental principle of gas sensitive resistor is extremely simple with the sensing elements deployed between 1 pair of electrodes .Even small extensions of this function can lead to considerable increases in the quantity and quality of the information derived about atmospheres containing for eg. A mixture of gases. This should be achievable through the use of more than 2 electrodes.

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