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Review Article

Metal Oxide Thin Films for Chemical and UV Sensors

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Abstract

Highly sensitive and fast responding Titanium Dioxide (TiO_2) nano sensors are developed for CO gas and other materials such as methanol and methane. Nano-porous TiO_2 thin films are prepared from a colloidal solution of TiO_2 nano particles (P-25) in ethanol by spray pyrolysis deposition (SPD) technique. Initially the TiO_2 films are grown at 60 ^{0}C and after the deposition, backed in an oven at 65 ^{0}C overnight and then annealed at 450 ^{0}C for one hour to get anatase phase. The surface morphology and structural properties of the films are studied using SEM and XRD. For sensor applications, two gold contacts separated by 0.25 mm are made on quartz substrate. A sensing and testing system has been developed based on change in the resistance of the TiO_2 film. CO gas (2% in Air) through mass flow controller is used for repeated five minutes cycles of air and CO at different temperatures in the range of 200 ^{0}C to 350 ^{0}C. Response and sensitivity of the sensor has been studied. Same apparatus and sensor is also used to detect UV, methane and methanol respectively.

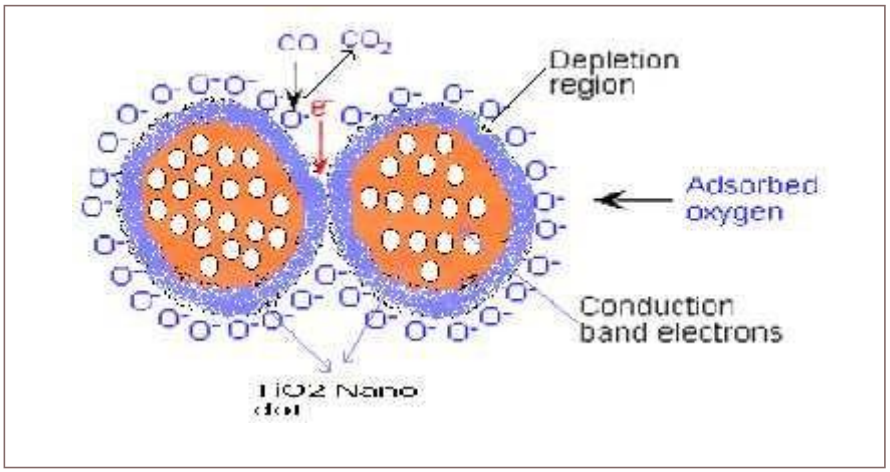
Keyword: Sensor; TiO2 Thin Films; Colloidal Solution; CO; UV; Methane; Methanol; Resistance

Introduction

Titanium-based systems for gas sensing belong to the semiconductor class of sensors, in which the resistance of the semiconductor is sensitive to the presence of a combustible gas [1-5].The basic mechanism utilizes the presence of Schottky barrier at the grain- boundaries in a poorly sintered body, porous or nano-porous thin films or thick films, where the grains are loosely in contact and the surface layer overlaps at the neck. Fig 1 illustrates this type of mechanism, using an n-type semiconducting oxide as an example. Firstly, oxygen from the ambient environment adsorbs in the surface of the grains, extracting an electron from the material, ionizes to O- or O-2; O- is believed to be dominant. This leads to formation of a depletion region and the conduction is determined by height of the barrier (qVs) at the intergranular contacts. In the presence of carbon mono oxide this negative oxygen ion converts it-self into carbon dioxide leaving behind an electron in the conduction band of TiO2. Presence of these electrons decreases the resistance of the TiO2 films. There are different methods of preparing nano-porous thin films [3-5]. Spray deposition is a fast growing materials processing technique adaptable to mass production. Widely used spray deposition method is selected for this research work due to its uniformity, good adherence, and crack-free results of the films, which are not possible in the common techniques like doctor blading, vacuum coating, dip coating, screen printing

[6-8]. To form a continuous nano particle network with sufficient adherence and electrical contact to the substrate, the nano particles deposited films are then subjected to post-treatment. A mixture of TiO2 nano particles and ethanol [9-12] or water [13-15] has often been used.

Figure (1): CO sensing mechanism in TiO_2 spray deposited films



Reaction: $CO + O^- \text{ ------> } CO_2 + e^-$ $CO + O \text{--------> } CO_2 + e^-$

Nano porous Titanium Dioxide has been chosen, for sensor applications because its bulk material is widely used for sensors and other applications [16-18]. Recently its nano particles, nano wires and nano belts were used in variety of different applications, where surface / interface properties play an important role [19- 21].

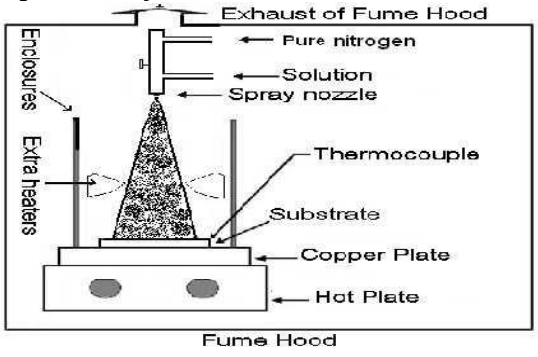
CO, CH_3OH and CH4 gases are causing environmental pollution, badly affecting the living beings. These gases are highly toxic; CO does not have any smell, therefore efficient sensor are need of the time in order to save the living being from their inverse effects. This was the main reason to initiate this work on TiO2, which is considered as one of the best candidate for these sensing applications. In order to improve the efficiency, porosity of the material was increased by using spray pyrolysis technique.

Experimental Details

Spray Pyrolysis Deposition Technique

Spray pyrolysis deposition technique involves the following steps; preparation of colloidal suspension containing TiO2 nano powder, cleaning of glass substrates in ultrasonic bath, spray deposition and drying and annealing of the films. 5% nano-crystalline TiO2 powder (with particle size of 25 nm from Degussa German) and 95% ethanol were mixed followed by stirring with magnetic stirrer for half an hour to prepare the TiO2 colloidal suspension. Glass substrates of size 1 x 1 inches were cleaned in an ultrasonic bath using iso-propyl alcohol (IPA) for 30 minutes. After cleaning, the substrates were dried in ambient temperature. Just after ultrasonic cleaning, glass substrates were laid on the hot plate at 60 0C for 30 seconds. The TiO2 suspension was sprayed onto the glass substrates with spray gun (Model No. 155-7 Anthum USA) connected to a pure compressed Nitrogen gas cylinder. The block diagram of the spray system is shown in the Fig. 2 [6-7]. The grown films on the glass substrates were kept in an oven at 65 0C for drying overnight. This drying process is necessary to take out all the ethanol in the films and to make it porous. After drying, the films were annealed at a temperature of 450 0C for one hour to produce the required anatase phase in the films and to enhance adherence with the substrate [12].

Figure (2): Schematic diagram of spray deposition system.



There were four parameters for spray deposition namely pressure of carrier gas (N2), temperature of the substrates, time for deposition and distance between spray gun nozzle and the glass substrate. Out of these parameters, distance, pressure and temperature were kept constant while the time of deposition (thickness) was variable. All the spray deposited samples and their parameters are given in (Table 1). A rotatable substrate holder has a magnetic stirrer attached to its bottom for rotation on the hot plate. There was an opening (mask) for the deposition of desirable size of the film on the glass substrate. Whole spray system was placed in a fume hood as shown in (Figure 2). Spray was done for various times as given in (Table 1) with 10 seconds interval.

Table (1): Deposition parameters. Note that thicker films were grown for 10 second intervals with 10 seconds delay in between them.

Sr. #	Sample #	Pressure (psi)	Temperature (^{0}C)	Time (sec)	Distance (cm)	Thickness (Å)
1	1TiO_2	25	60	30	20	1000
2	2TiO_2	25	60	40	20	1600
3	3TiO_2	25	60	50	20	1700
4	4TiO2	25	60	20	20	700
5	5TiO2	25	60	10	20	350
6	6TiO2 (CO sensor)	25	60	70	20	2100
7	7TiO2 (other sensors)	25	60	35	20	1200

Scanning electron microscope (SEM) model SU-1500 (Japan) was used to study the surface morphology, while X-ray diffraction (XRD) model "PANalytical Xpert, Pro Holland" with Cu Kα radiation λ = 1.5418 Å) with operating conditions voltage/current 40 kV/30mA and scan speed 81/min was used for checking the phases of TiO2 present in the films. Thickness of the deposited films was measured with optical microscope.model Zeiss Axio M1.

Sensor Construction

After making sure that the TiO2 films were nano/micro porous and of anatase phase using SEM and XRD results respectively, the sensors were made as described below. Thin quartz substrate (0.30 mm thick) with two gold evaporated contacts, (having a separation of 0.25 mm) has been used to fabricate sensor TiO2 film with the help of a metal mask of size 10 mm x 4 mm over the separation of the gold contacts. This gold coated quartz substrate was attached to the rotatable sample holder and placed on the hot plate and its rotation was set at around 10 revolutions per second. The temperature of the substrate holder was kept at 60 0C. Using spray gun, the TiO2 colloidal solution was sprayed for 10 sec. Then the spray was stopped for 10 sec. After 10 sec interval, spray was resumed again for 10 sec. In this way, a thick film 6TiO2 (of 50 seconds in 5 intervals of 10 seconds with 10 seconds delay time in each spray) has been made. This sensor was backed overnight at 65 0C and then annealed at 450 0C for one hour. Some other sensors with different thicknesses were also made.

Apparatus for testing the Sensor for CO, Methane and Methanol

A piece of marble having 30 mm width and 75 mm length with two pressure contacts of copper, was used to hold the sample tightly. Two copper wires covered with ceramic beads were attached to pressure contacts. This sample was kept into a quartz tube having 30 mm diameter and 200 mm of length.

Two ends of quartz tube were closed with silicon corks. From one end of the quartz tube, connection of the CO/ethane/methanol gas and air was made. CO gas was provided through mass flow controller (MFC).While the air /methane and methanol were controlled by a gas flow meter. Exhaust line was provided from the other end of the quartz tube. A K-type thermocouple was also attached near the

sensor to find the actual temperature of the sensor. A complete block diagram of the sensor testing system has been given at (Figure 3). A cylinder of 2% CO and 98% air was used to test the sensor.

Figure (3a): Shows schematic diagram of sensor testing system

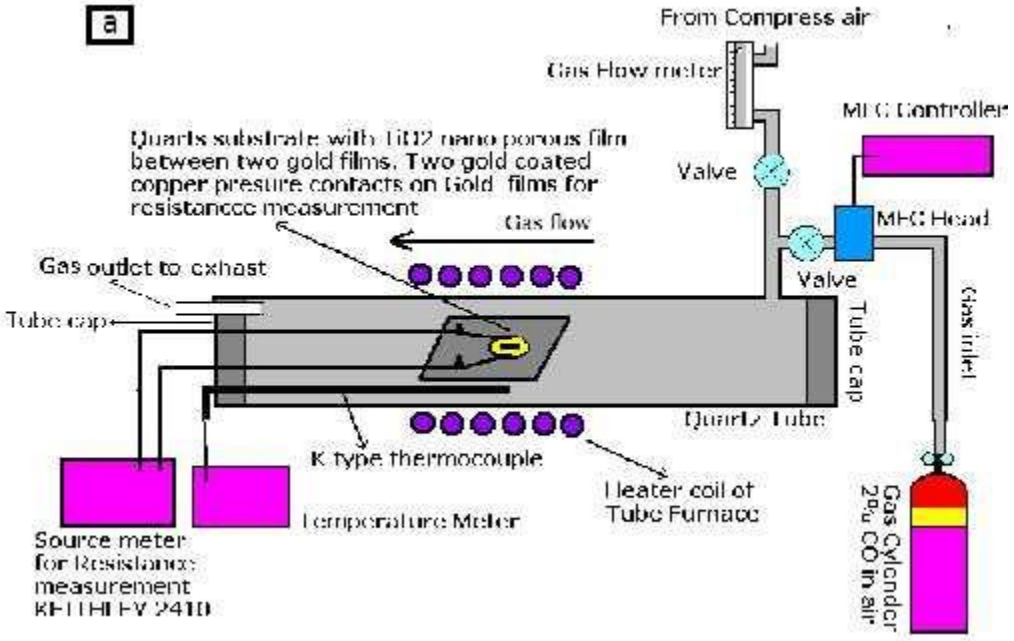


Figure (3b): Metal contacts on sensor for resistance measurements

Quartz tube with sensor was placed in tube furnace to provide temperature in the range of 200 0C to 350 0C. In order to measure the resistance, a Keithley source meter (Model 2410) was used. Two connections from the copper contacts were connected to Keithley source meter.

Sensor resistance variations with time during CO/Ethane/Methanol and air cycles

After making sure that all the connections of gases were tight and all electric connection were made, the temperature of the furnace was set to desirable value. The temperature of the sensor inside the tube was separately monitored using a K- type thermocouple. After reaching the desirable temperature inside the quartz tube at the sensor, compressed air valve was opened and maintained at the desirable pressure using a flow meter. Compressed air was kept for an interval of five minutes. After five minutes, the compressed air valve was closed and the valve of either CO/ethane/methanol gas was opened. CO gas flow rate was fixed to 50 SCCM while pressure of ethane or methanol was kept at 100 SCCM. In this way a cycle of five minutes of air and five minutes of gas has been maintained. The resistance of the sensor was continuously measured during these cycles of air and gas.

Results and Discussion

Structural Analysis

(Figure 4) indicating the XRD results for the samples 1TiO2 to 5TiO2, which were deposited for various time, ranging from10 sec to 50 sec, keeping other parameters like substrate temperature, carrier gas pressure and distance between spray gun and glass substrate remained constant. All TiO2 films showing anatase (101) preferred phase along with other small anatase phases [12]. (Figure 5) indicates SEM results with following details ;(a) Film 5TiO2 with magnification of 5000 at 50 µm scale, (b) Film 5TiO2 with 1000 magnification at 10 µm scale. (c) Film 3TiO2 with 5000 magnification at 50 µm scale (d) Film 3TiO2 with 5000 magnification at 50 µm scale. These four micro graphs of the films 5TiO2 and 3TiO2 indicate that the surface porosity is in the range of micro to nano porous with average particle size of 10 to 50 µm. This large porosity is very important to increase surface area of the film. Large surface area will absorb more CO gas in it and hence sensitivity of the sensor will be increased.

Figure (4): XRD results of TiO2 spray deposited films and nano powder

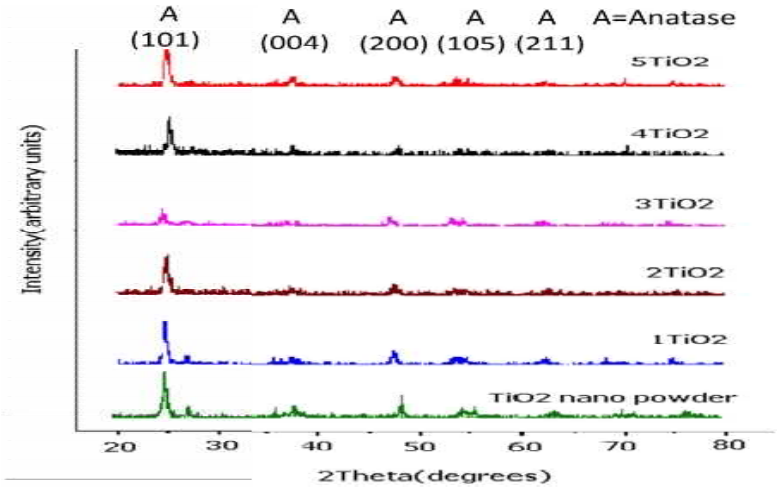
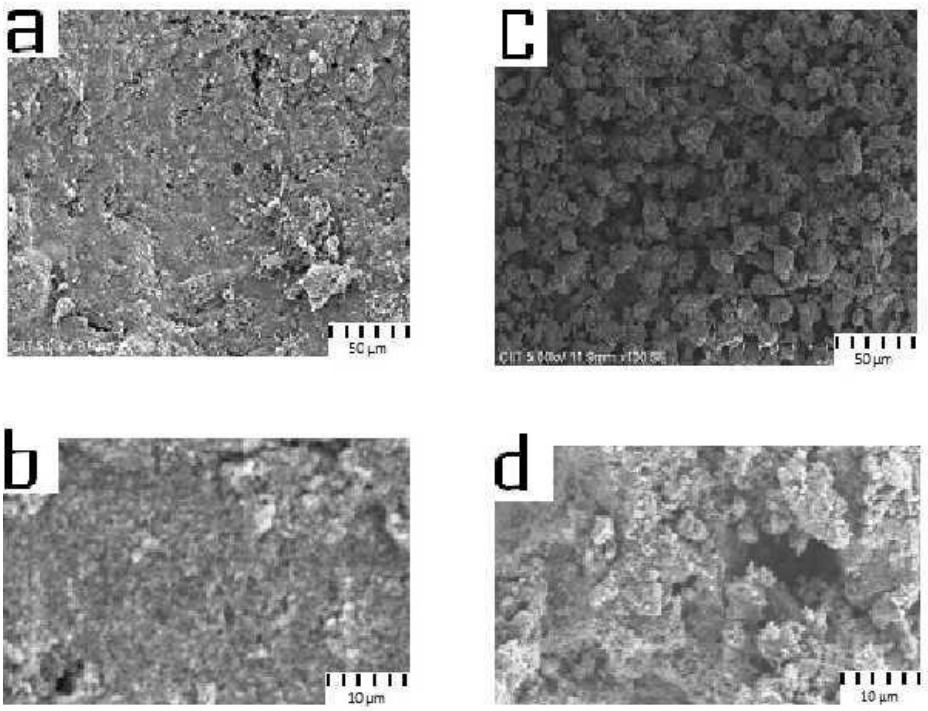


Figure (5): SEM micrographs of 5TiO2 Films (a and b) and 3TiO2 Films (c and d)



CO Sensing Results

A graph of resistance Vs time of the sensor has been given in (Figure 6 (A)) for sensing of Carbon Mono-Oxide (CO) at a constant temperature (270 0C) with the cycle of Air and CO of 5 minutes interval each. Resistance measurements were stopped after seven cycles of air and six cycles for CO. Resistance measurement were started and ended with compressed air. First 5 minute interval shows the resistance with Air and next 5 minute interval shows the resistance with CO which is smaller due to absorption of electrons in the TiO2 film from the oxygen ions. The upper points of all the cycles in the graph showed the resistance of the sensor with compressed air and lower points showed the resistance of sensor in presence of CO. The average sensitivity and average response time of CO sensor and for methane, methanol and UV are given in (Table 3).

Other Sensing Results

UV, methane and methanol sensing has also been carried out with the nano-porous TiO2 sensor. Their resistance Vs time graphs are presented in Fig. 6 (B, C and D). Complete Gas sensing parameters of nano-porous TiO2 sensors for CO, UV, Methane and Methanol are given in (Table 2). Sensitivity and response time of all sensors is given in (Table 3).

Table (2): Parameters of TiO2 sensor films for UV, Methane and Methanol sensing.

Sensing source	Sensor Thickness (Å)	Interval	Gas Pressure (SCCM)	Air Pressure (SCCM)	Sensor Temperature (^oC)
Carbon Monoxide (CO)	2500 À	5 min Air 5 min Gas	50 SCCM	100 SCCM	270
Methane (C_2H_5OH)	1200 À	5 min Air 5 min Gas	100 SCCM	100 SCCM	300-350
Methanol (CH_4)	1200 À	5 min Air 5 min Gas	100 SCCM	100 SCCM	300-350
UV (4V, 18w) (300 – 367)nm	1200 À	2min on 2min off	----------	----------	Room Temp.

Figure (6): Variation in resistance of the sensor with time. (A) For CO, (B) For Methane, (C) For Methanol (D) For UV light.

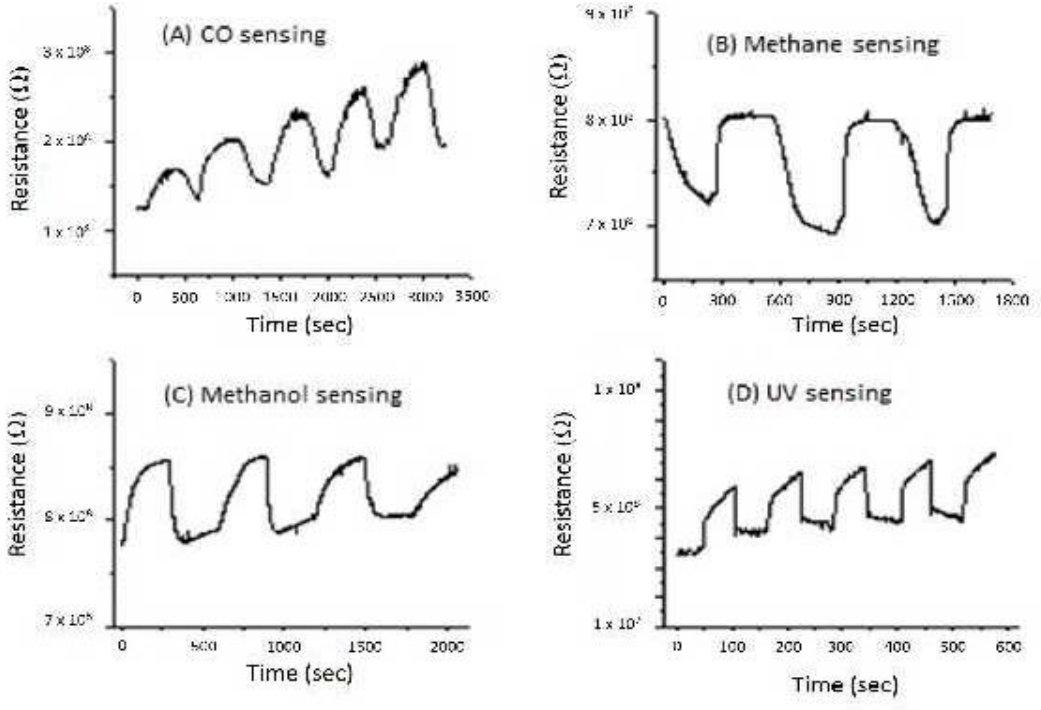


Table (3): Sensitivity and response time for the sensors

Sensor	Average Sensitivity	Average Response time
Carbon monoxide (CO)	1.79	205.30 Sec.
Methane (C_2H_5OH)	1.13	141.89 Sec.
Methanol (CH_4)	1.09	81.54 Sec.
UV (4V, 18w, Phillips bulb)	1.28	3.79 Sec.

Conclusions

Crystalline nano-powder of TiO_2 in absolute ethanol was used to deposit films on to hot glass substrates by low cost spray technique successfully. XRD of TiO_2 films confirms that they are anatase (101) phase and the surface structure examined by SEM indicated that the surface is nano/micro porous and hence the surface area has been increased many fold by this technique. Testing of the sensors at 270 ^{0}C in the five minutes cycles of air and CO showed the decrease in resistance during CO and reversing of the resistance to higher values when air is flown. An average sensitivity of 1.79 and an average response time of 275.3 seconds were achieved in these sensors. However the sensitivity of CO sensor is smaller than the sensor made from the same material for UV, Methane and methanol sensors. The response time of UV sensor at room temperature was small as compare to sensors of the same material for CO, Methane and Methanol tested at elevated temperatures. It was seen in all the sensors that sensitivity was increasing with time. This may be due to two reasons namely the increase of the resistance of copper contacts on sensor due to higher temperature and increase of resistance of the copper contacts due to oxidation at higher temperatures. There were no oxidation issues with film or gold contacts.

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