ISSN 1726-5479

SENSORS & TRANSDUCERS

vol. 120
9 /10

TEDS Sensors, IEEE 1451 Standards

International Frequency Sensor Association Publishing

IFSA

Sensors & Transducers

Volume 120, Issue 9, September 2010 **www.sensorsportal.com** **ISSN 1726-5479**

Sensors & Transducers Journal (ISSN 1726-5479) is a peer review international journal published monthly online by International Frequency Sensor Association (IFSA).
Available in electronic and on CD.

Sensors & Transducers Journal

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Volume 120
Issue 9
September 2010

www.sensorsportal.com

ISSN 1726-5479

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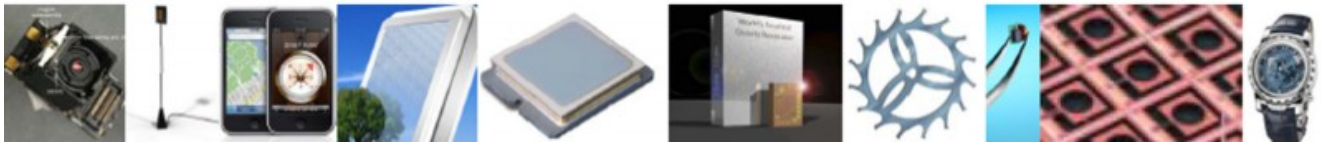

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ICONS 2011

January 23-28, 2011 - St. Maarten,
The Netherlands Antilles

Important deadlines:

Submission (full paper)	September 25, 2010
Notification	October 20, 2010
Registration	November 5, 2010
Camera ready	November 5, 2010

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- EDNA: Emergency Services and Disaster Recovery of Networks and Applications
- IPv6DFI: Deploying the Future Infrastructure
- IPDy: Internet Packet Dynamics
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- Advanced biocomputation technologies
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- Bioimaging
- Neuroinformatics

B. Computational systems
- Bio-ontologies and semantics
- Biocomputing
- Genetics
- Molecular and Cellular Biology
- Microbiology

C. Biotechnologies and biomanufacturing
- Fundamentals in biotechnologies
- Biodevices
- Biomedical technologies
- Biological technologies
- Biomanufacturing

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Sensors & Transducers Journal, Vol. 120, Issue 9, September 2010, pp. 38-52

www.sensorsportal.com

Sensors & Transducers

ISSN 1726-5479

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Gas Sensing Properties of Pure and Cr Activated WO_3 Thick Film Resistors

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Received:8 June 2010 /Accepted: 14 September 2010 /Published: 27 September 2010

Abstract: Thick films of WO_3 (Tungsten Oxide) were prepared by screen-printing techniques. The surfaces of the films were modified by dipping them into an aqueous solution of Chromium Oxide (CrO_3) for different intervals of time, followed by firing at 550 ^oC for 30 min. The gas sensing performance of the pure and Cr_2O_3-modified films was tested for various gases at different temperatures. The unmodified films showed response to H_2S, ethanol and cigar smoke. However Cr_2O_3- modified films suppresses gas sensing response to all gases except H_2S. The surface modification, using dipping process, altered the adsorbate-adsorbent interactions, which gave the specific selectivity and enhanced sensitivity to H_2S gas. The gas response, selectivity, thermal stability and recovery time of the sensor were measured and presented. The role played by surface chromium species to improve gas sensing performance is discussed.

Keywords: WO_3 thick film, Cr_2O_3-modified films, H_2S gas sensor, thick films, selectivity, response and recovery time.

1. Introduction

Gas sensors are playing an increasingly important role in environmental monitoring, control of chemical processes, remote sensing, space, agricultural and medical applications. Generally, any gas sensor must possess two basic functions receptor and transducer. In the semiconductor gas sensors, the receptor function is provided by the interaction of the semiconductor surface with an object gas via gas

adsorption and surface reactions, while the transducer function depends not only on the band structure of the semiconducting oxide but also on the microstructure of the coagulating particles [1]. Recently, there is an increasing need for the detection of toxic, polluting and smelling gases at low levels in air. For such low-level gases, sensors should be sufficiently upgraded in sensitivity and selectivity, and especially important is the promotion of the receptor function, as suggested from the reported examples of sensor modifications brought about by the addition of noble metals [1, 2], metal oxides [3-5] or surface fictionalizations [6-10].

Chemical sensing of gases is crucial for a number of environmental applications, and a vast number of sensor materials have been developed. Normally, they can be used for detecting individual gases. For recording of fungal volatiles in the food industry-it is common to use sensor arrays commonly referred to as "Electronic noses". Their operating principle is that adsorption of species on to the surface of sensor material produces reaction heat or altered surface properties. These properties are frequently optical and electrical ones. Electrical detection has an advantage in its simplicity and in the inherent ability to integrate signals. In order to improve the performance of the devices, it is crucial to increase the surface area of the sensor and / or to enhance the signal of the electrical response of the device.

Metal oxide semiconductors-such as WO_3, TiO_2, ZnO and SnO_2 are widely used in sensors having high detection ability and stability [12, 13]. It is also known that noble metal dopants (Au, Pt, and Pd) can be used to increase the sensitivity of an oxide sensor [14]. Focusing only at the most recent work, we note that WO_3 can be employed for detecting hazardous pollutants such as H_2S [15, 16] and NOx [16-22]. Other gases- for example alcohol, CHx, CO, NH_3-can be detected by WO_3 Sensors as well [18, 19, 23]

WO_3 thick film sensors have drawn considerable interest because of their good electrical and optical properties, in combination with their wide band gap, n-type of conductivity, abundance in nature and absence of toxicity.

Hydrogen sulfide is a toxic, corrosive and inflammable gas, which is produced in sewage, coal mines, oil and natural gas industries, etc and is utilized in many chemical industries. There are two general forms of H_2S poisoning [11], subacute and acute. **Subacute poisoning**: the odor of H_2S can be perceived at levels as low as 10 ppb. Breathing air or gas containing H_2S at 10 to 500 mole ppm for an hour or more may cause subacute or chronic poisoning, and may cause the sense of smell to fail. The symptoms of subacute poisoning are headache, inflammation of the eyes and throat, dizziness, indigestion, excessive saliva and weariness. These can also be the result of continued exposure to H_2S in low concentration, and edema to the lungs may also occur.

Acute poisoning: breathing air or gas containing more than 500 mole ppm of H_2S can cause acute poisoning and can possibly be fatal. The symptoms of acute H_2S poisoning are muscular spasms, irregular breathing, lowered pulse, odor to the breath and nausea. Loss of consciousness and suspension of respiration quickly follow. Even after the victim recovers, there is still risk of edema to the lungs, which may cause severe illness or death within 8 to 48 hours. When one breathes in H_2S, it goes directly into lungs and is absorbed into the blood stream. Free H_2S in the blood reduces its oxygen carrying capacity, thereby depressing the nervous system. H_2S is quickly oxidized into sulfate in the body. If one breathes so much H_2S that the body can not oxidize all of it, then H_2S concentrates in the blood, and the person becomes poisoned. The nervous centers in the brain that controls breathing are paralyzed.

Toxic gas detection has gained increasing prominence, due largely to greater concerned over safety and the consequent introduction of legislation. Surprisingly there are still relatively few viable sensors available for gases such as chlorine, ammonia, nitrogen dioxide and hydrogen sulfide. Most of the studies on solid state semiconducting gas sensors used as chemi-resisters have concentrated on

flammable gases. However, the same principles that are practiced in flammable gas sensing can be applied to toxic gas sensing and in some, but not all, cases the toxic gas itself may be involved in combustion. Earlier work by several authors [24, 25] has shown the potential of several novel solid state semiconducting materials as viable gas sensing materials. Most of these materials are based on mix metal oxides with a dominant crystal structure that may change when the stoichiometric proportion of the metal centers is altered. When heated to elevate temperatures greater the 200 ^{o}C the mixed metal oxides exhibit intrinsic semi conducting behavior giving either p or n type conduction. In most cases the resistance change which is observed when a gas is applied to these materials depends on the oxidative or reductive nature of the gas and the type of semiconductor under test.

The semiconducting oxides such as ZnO_2, SnO_2, Fe_2O_3, Ga_2O_3, Sb_2O_3 [26-32], etc are sensitive to toxic and inflammable gases. It has also reported the surface additives play important role in enhancing the gas response [33-37] and specificity to a particular gas. The additives like Al, In, Cu, Fe, Sn, Ru [38, 39] are often added to improve the response and selectivity.

In the present article thick film surfaces are modified by doping them in to 0.1M solution of CrO_3 for different time intervals, followed by firing. Firing would convert the CrO_3 into Cr_2O_3. In the surface modification process, the grains of Cr_2O_3 would disperse on the grains of WO_3. The dipping techniques increase the surface to volume ratio of the sensor. Investigations are carried out on pure Tungsten Oxide (WO_3) and Cr_2O_3-modified WO_3. Unmodified WO_3 showed response to different gases at different operating temperatures. For example, it selects cigar smoke at 300 ^{o}C, H_2S at 350 ^{o}C, and ethanol at 450 ^{o}C. However, the response of the Cr_2O_3-modified WO_3 film is exceptional, interesting and unique. It showed selective response to H_2S only by suppressing the responses to other gases. Also response to H_2S is shifted from 350 ^{o}C to 250 ^{o}C. The key role played by the Cr_2O_3 misfit regions in case of Cr_2O_3-modified WO_3 film is discussed.

2. Experimental

2.1. Powder and Paste Preparation

The AR grade WO_3 powder (99.9 % pure) was milled for 2 h so as to obtain fine-grained powder. The powder was then calcinated at 1000 ^{o}C for 6h in air and re-ground. The thixotropic paste was formulated by mixing the fine powder of WO_3 with the solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and terpineol. The ratio of inorganic to organic part was kept at 75:25 in formulating the paste.

2.2. Preparation of Pure and Chrominated WO_3 Thick Films

This paste was screen printed [36, 37] on a glass substrate in a desired pattern. The as prepared films were fired at 550 ^{o}C for 30 min for removal of organic binders. The silver contacts were made for electrical measurements. The surface modified WO_3 thick films were obtained by dipping them in a 0.1 M aqueous solution of chromium oxide (CrO_3) for different dipping time intervals of 5, 10, 20 and 30 minutes. The films were dried at 80 ^{o}C, followed by firing at 550 ^{o}C for 30 min. These surface modified films are termed as 'chrominated' WO_3 films.

2.3. Thickness Measurements

The thickness of the films was observed in the range from 25 to 30 μm. The reproducibility in thickness of the films was possible by maintaining the proper rheology and thixotropy of the paste.

2.4. Details of Gas Sensing System

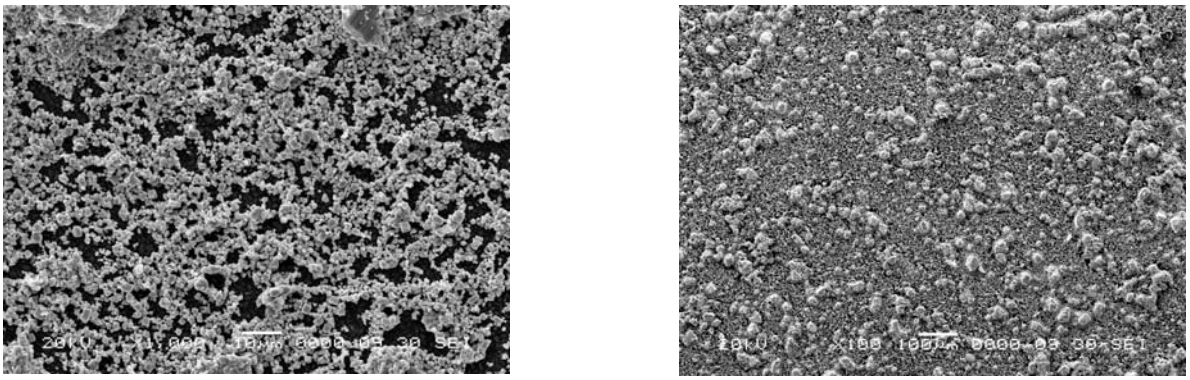
The sensing performance of the thick film sensors was examined using a 'static gas sensing system'. A heater was fixed on the base plate to heat the sample under test up to required operating temperatures. The Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of a test gas using a gas-injecting syringe. A constant voltage was applied to the sensor, and the current was measured by a digital picoammeter. Air was allowed to pass into the glass chamber after every gas exposure cycle.

3. Results and Discussion

3.1. Micro Structural Analysis

The micro structural and chemical compositions of the films were analyzed using a scanning electron microscope (SEM, JEOL JED 6300) coupled with an energy dispersive spectrometer (EDS, JEOL JED 2300LA).

Fig. 1 (a) depicts the SEM image of the unmodified WO_3 thick film fired at 550 ^oC. The film consists of randomly distributed grains with larger and wide range of grain size. Fig. 1 (b) is the SEM image of the Cr_2O_3-modified WO_3 film (20 min). It depicts that the microstructure of Cr_2O_3-modified film (20 min) consists of spherical particles of Cr-species distributed uniformly with smaller size and shape on the WO_3 grains. The smaller particle may be attributed to the Cr-misfits.



(a) (b)

Fig. 1. SEM images of: (a) unmodified; and (b) surface chrominated WO_3 films.

3.2. Elemental Analysis

The quantitative elemental composition of the unmodified and Cr_2O_3 modified WO_3 films were analyzed using an energy dispersive spectrometer.

Stoichiometric compositions of cations (W) and anions (O) are 52.00 and 48.00 wt%, respectively. The observed compositions of these constituent elements were not consistent with the stoichiometric proportion and all samples were observed to be the oxygen deficient, leading to the semiconducting nature of the WO_3.

It is clear from Table 1 that the weight percentage of Cr is increasing with dipping time. The modified film with a dipping time of 20 min is observed to be more oxygen-deficient (18.73 wt %). This oxygen deficiency may make the sample possible to adsorb a relatively larger amount of oxygen species.

Table 1. Elemental analysis.

Elements (Wt %)	**Dipping time (min)**				
	0	5	10	20	30
O	18.49	22.04	19.10	18.73	21.06
Cr	0	0.56	0.64	0.69	1.05
W	81.51	77.40	80.26	80.58	77.90

3.3. Thermal Properties

Thermo gravimetric (TGA) of the films were conducted in air using Mettler Toledo Star System-851 at a heating rate of $10^{o}C\ min^{-1}$ in the temperature range from room temperature to 900 ^{o}C with α-Al_2O_3 as the reference.

Fig. 2 shows the TGA profiles of pure and Cr_2O_3-modified WO_3 films. Table 2 lists losses or gains in weight of these films observed during TGA in the different temperature ranges. It could be concluded from the profiles that the Cr_2O_3-modified WO_3 was more stable than the pure WO_3. Comparatively a less weight loss in the Cr_2O_3-modified sample can be attributed to the adsorbed oxygen content. The modified film with the content of Cr (0.69 wt **%**) was observed to contain the smallest amount of oxygen (18.73 wt **%**, Table1), which could be attributed to the largest deficiency of oxygen in the film. It is, therefore, quite possible that the material would adsorb largest possible amount of oxygen, showing a relatively less loss in weight (0.70 w t **%**) in the temperature range of 25-600 ^{o}C.

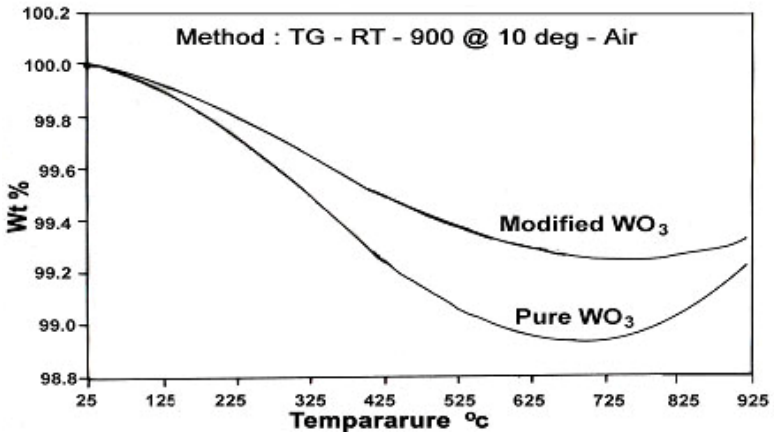


Fig. 2. TGA of unmodified and surface chrominated WO_3 film.

The smallest weight loss of Cr_2O_3-modified WO_3 may be due to its larger stability. The chromium oxide on the surface Cr_2O_3-modified sample would form misfit regions between the grains of WO_3 and could act as an efficient catalyst for oxygenation. Relatively modified WO_3 sample was found to be more stable than pure sample.

Table 2. Thermal analysis.

Temperature ^{0}C	Unmodified WO_3		Temperature ^{0}C	Cr_2O_3- WO_3	
	Loss (wt %)	Gain (wt %)		Loss (wt%)	Gain (wt %)
25 – 600	1.15	--	25 – 600	0.70	--
600 – 750	--	--	600 – 750	--	--
750 -900	--	0.3	750 -900	--	0.05

3.4 Electrical Properties

3.4.1 I-V Characteristics

I-V characteristics of pure and chrominated-WO_3 are observed to be linear and symmetrical in nature, indicating the ohmic nature of silver contacts. (Fig. 3).

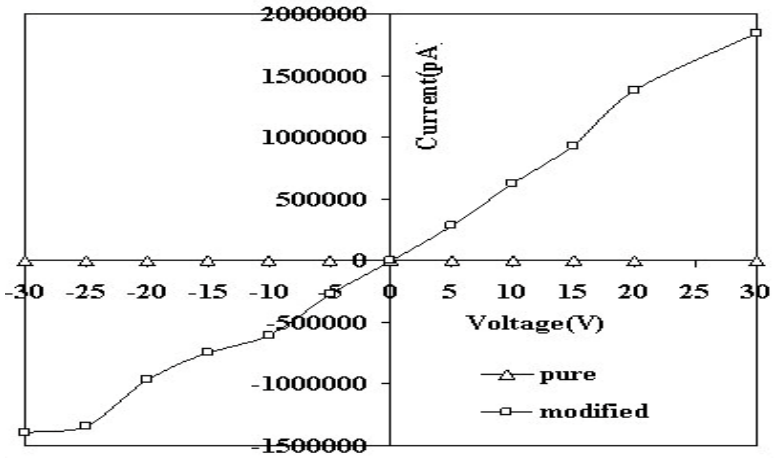


Fig. 3. I-V Characteristics of pure and surface chrominated WO_3 film.

3.4.2. Variation of Conductivity with Temperature

Fig. 4 depicts the conductivities of pure and modified WO_3 at room temperature. The conductivity of Cr_2O_3 modified WO_3 film was observed to be too much higher than that of pure WO_3 at room temperature. This could be attributed to the WO_3- Cr_2O_3 intergrain boundaries and hence intergranular potential barrier. Cr_2O_3 grains may reside in inter granular regions of WO_3, Resulting in formation of inter grain boundaries and the reduction of inter granular potential barrier.

Fig. 4 and Fig. 5 show the dependence of electrical conductivity with temperature of unmodified and chrominated-modified WO_3 film for the dipping time interval of 5, 10, 20 and 30 min in air and H_2S environment. Conductivity of these films goes on increasing with an increase in temperature. Hence resistivity goes on decreasing with increase of temperature. Therefore, both unmodified and modified material exhibit negative temperature coefficient of resistance (NTC).

Both unmodified and modified samples in H_2S ambient show negative temperature coefficient behavior in operating temperature range from 100 ^{0}C to 450 ^{0}C. Increase in conductivity in H_2S ambient could be attributed to the reducing nature of H_2S, which is oxidized by the negatively charged surface oxygen species, resulting in the release of the trapped electrons.

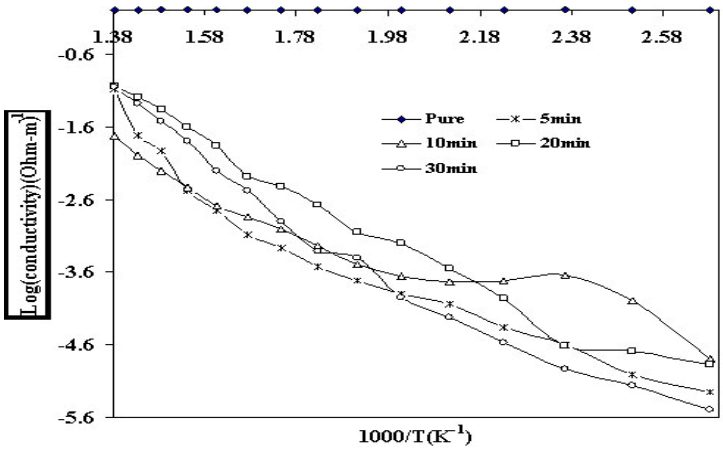


Fig. 4. Variation of conductivity with temperature in air environment.

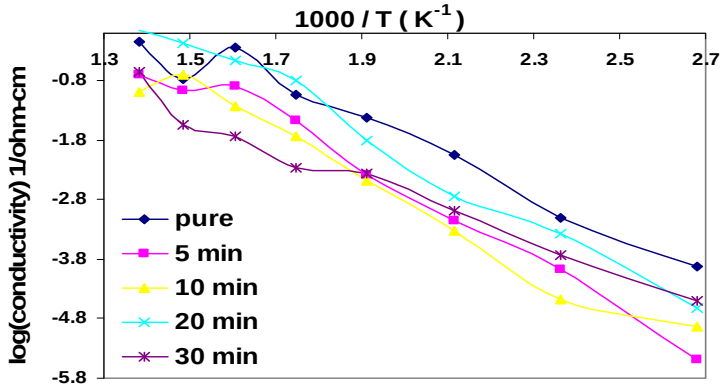


Fig. 5. Variation of conductivity with temperature in H_2S environment.

4. Gas Sensing Performance

4.1. Gas Sensing Characteristics

Gas response (S) is defined as the ratio of change in conductance of a sensor on exposure to a test gas to the conductance in air.

$$S = \frac{Gg - Ga}{Ga} = \frac{\Delta G}{Ga},$$

where Ga and Gg are the conductance of sensor in air and in the test gas medium, respectively.

Selectivity is defined as the ability of a sensor to respond to certain gas in the presence of other gases. The selectivity coefficient in percentage [40] can be calculated as follows:

$$\% \text{ Selectivity} = \frac{S}{S_{target\ gas}} X\ 100,$$

where S is the response to a particular gas and $S_{target\ gas}$ is the response of the gas to be selected/sensed from a mixture of various gases.

The time taken for the sensor to attain 90% of the maximum change in resistance on exposure to a test gas is the response time. The time taken by the sensor to get back 90% of the original resistance is the recovery time [40].

4.2. Response of Unmodified WO_3 film to Various Gases at Different Temperatures

Fig. 6 shows the variation of gas response of the unmodified WO_3 films to various gases (400 ppm) with operating temperature ranging from 100 to 450 ^oC. For H_2S, the response goes on increasing with operating temperature, attains its maximum (191.31) at 350 ^oC and then decreases with a further increase in operating temperature. It is clear from the graph that, the sensor also gives the maximum response to ethanol (89.95) at 400^oC and cigar smoke (47.12) at 300 ^oC.

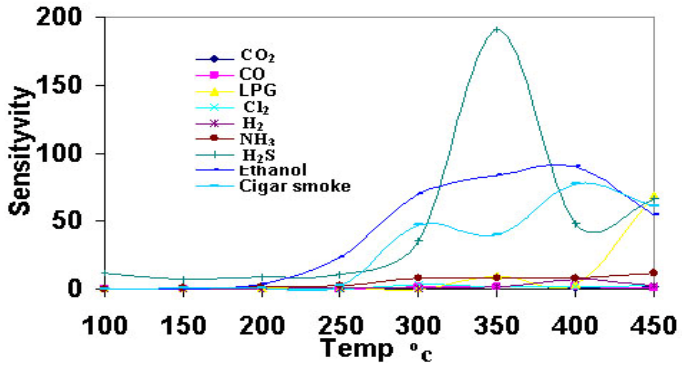


Fig. 6. The response of the unmodified WO_3 sensor to various gases.

The sensor selects a particular gas at a particular temperature. Thus by setting the temperature, one can use the sensor for particular gas detection. The same sensor could be used for the detection of different gases by operating it at particular temperature for a typical gas. This can be attributed to different chemical reactivity's of different gases on the sensor surface. Different gases have different energies for adsorption, desorption, and reaction on the metal oxide surface, and therefore the response of the sensor at different temperatures would depend on the gas being sensed.

The amount of oxygen adsorbed (O_2^-, O^-, O^{2-}) on the sensor surface goes on increasing with an increase in temperature, reaches to the maximum and then decreases with a further increase in operating temperature. The response to the gas to be detected follows the same behavior. When a reducing gas comes in contact with the sensor surface, it gets oxidized. The rate of oxidation would be the function of the amount of adsorbed oxygen on the surface and the type of gas to be detected. The larger the rate of oxidation, the larger would be the number of electrons released, and in turn the larger would be the gas response. At higher temperatures (beyond about 350 ^0C), the amount of oxygen adsorbed would be smaller, leading to a slower rate of reduction of a target gas and, therefore, the smaller gas response.

4.3. Percentage Selectivity of Unmodified WO_3 Film at Various Operating Temperatures

Fig. 7 shows the histogram indicating the variation of the percentage selectivity coefficient with operating temperature of the unmodified WO_3 film for various gases.

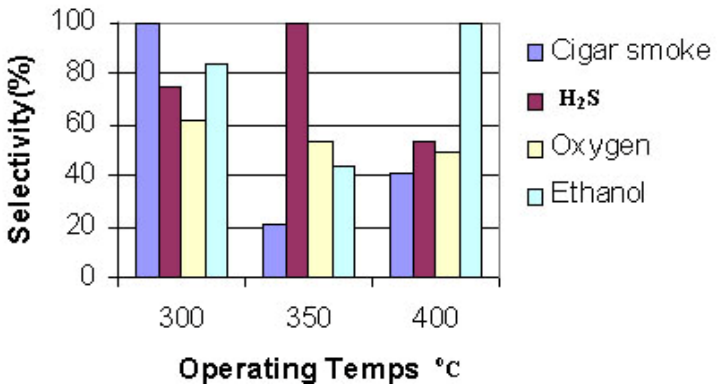


Fig. 7. Percentage selectivity of the unmodified WO_3 sensor to various Gases.

Histogram depicts that the sensor selects a particular gas at a particular temperature. The sensor would be a cigar smoke sensor at 300 ^oC, a H_2S sensor at 350 ^oC, and an ethanol gas sensor at 400 ^oC. This behavior could be attributed to the unique receptor function at a particular temperature, that is, different capability of the WO_3 multi component sensor to recognize and select an objective gas from other gases.

4.4. Response of Modified WO_3 Film

Fig. 8 represents the variation of sensitivity to H_2S gas at different operating temperatures for unmodified and Cr_2O_3-modified WO_3 films dipped for 5, 10, 20 and 30 min. Maximum response to H_2S gas was observed for Cr_2O_3 modified WO_3 film dipped in 0.1 M solution for 20 min.

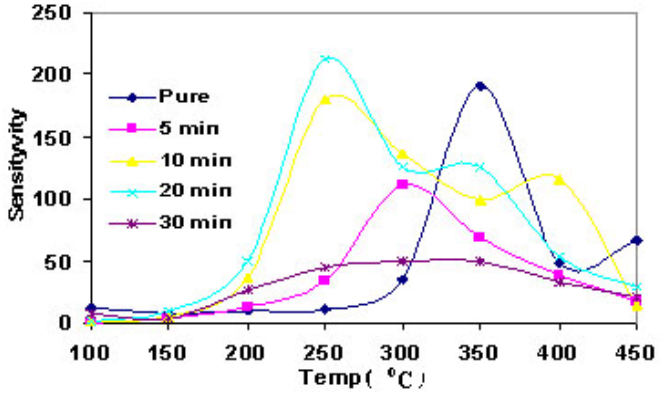


Fig. 8. Sensitivity of pure and modified WO_3 films to H_2S gas.

Fig. 9 represents the variation of sensitivity to various gases at different operating temperatures for Cr_2O_3-modified WO_3 film dipped in 0.1M solution for 20 min. Graph shows that modified film is sensitive to H_2S gas only and suppresses response to other gases. Also response to H_2S is shifted from 350 ^0C to 250 ^0C.

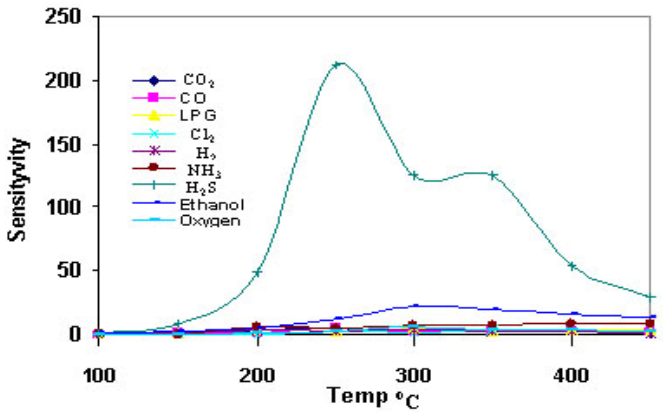
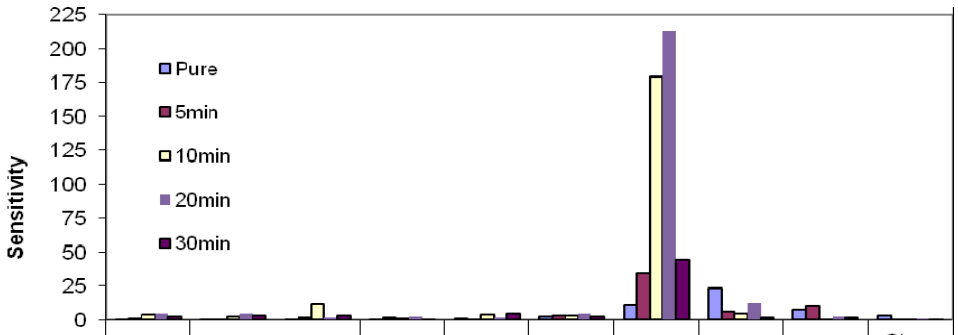


Fig. 9. Sensitivity of modified WO_3 film dipped in 0.1 M solution for 20 min .

4.5. Selectivity of Cr_2O_3 Modified WO_3 Film

The selectivity of modified film to H_2S gas against other gases at 250 ^{0}C is shown in Fig. 10.



	CO2	CO	LPG	Cl2	H2	NH3	H2S	Ethanol	O2	Cigar Smoke
Pure	0.2787	0.2879	0.5	0.0214	0.8406	2.6933	10.862	23.873	7.4	3.0303
5min	0.78	0.36	1.82	1.8	0.12	2.98	34.2	6.22	10.78	0.3
10min	4.08	2.59	11.9	0.85	3.62	3.1	179.5	5.04	0.44	0.21
20min	4.49	4.33	1.84	2.48	2.13	5.05	212.34	12.6	2.64	1
30min	2.78	3.16	3	0.58	5.05	2.83	44.63	1.86	1.8	0.27

Fig. 10. Selectivity of modified film to H_2S gas against other gases at 250 ^{0}C.

4.6. Variation of Response of Modified Film with H_2S Gas Concentration

Fig. 11 depicts variation of sensitivity with H_2S gas concentrations at 350 ^{0}C for unmodified and Cr_2O_3 modified WO_3 film dipped in 0.1 M solution for 20 min at 250 ^{0}C.

It is clear from the Fig. (11) and that, the gas response increases with the H_2S gas concentration, attains the maximum at 520 ppm and 280 ppm concetration for unmodified and Cr_2O_3 modified WO_3 sensor respectfully. The response decreases with further increase of gas concentration. The excess gas would form multimolecular layer on the film surface and the part of gas amount would be idle and unable to interact with sensor surfaces. Hence response would decrease further.

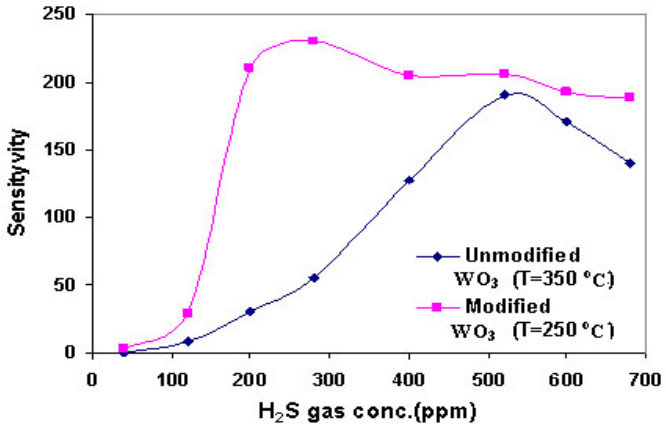


Fig. 11. Variation of response to H_2S at different concentration.

4.7 Response and Recovery Time

Fig. 12 shows the variations in response to H_2S (40 ppm) with time for the modified WO_3 film at 250 ^oC. The 90 % response and recovery levels were attained within 3 s and 7 s, respectively. The fast response and recovery times are the attractive features of the Cr_2O_3-modified WO_3 sensor.

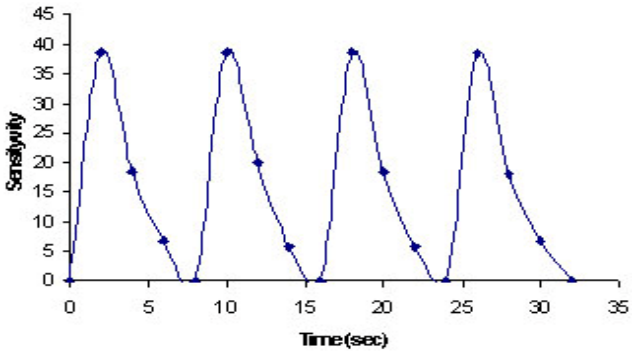


Fig. 12. Response transients of the Cr_2O_3 modified WO_3 film to H_2S.

5. Discussion

The surface chrominated modified films are looked upon as the small particles of chromium oxide distributed along the grain boundaries of WO_3. CrO_3 on the surface of WO_3 film is not thermally stable above its melting temperature (197 ^0C) losing oxygen to give, after series of intermediate stages, Cr_2O_3 [41]. In this investigation sensors are tested in the operating temperature range from 100 to 450 ^0C so that at 200 ^0C, some CrO_3 would convert in to Cr_2O_3. Some amount of CrO_3 may also be reduced into Cr_2O_3 by trapping electrons from the oxygen vacancies in WO_3 material. Local oxygen deficiency may trigger the reaction:

On exposure to H_2S gas, Cr_2O_3 would convert would be converted into Cr_2S or CrS, which are known to be metallic in nature and more conducting than Cr_2O_3. On exposure to H_2S gas on the chrominated WO_3, the sensor resistance decreases suddenly giving higher sensitivity. This can be represented as:

$$2Cr_2O_3 + 2H_2S \rightarrow 4CrO + SO_2 \quad (1)$$

$$CrO + H_2S \rightarrow CrS + H_2O \quad (2)$$

$$Cr_2O_3 + 3H_2S \rightarrow Cr_2S_3 + 3H_2O \quad (3)$$

On subsequent exposure of sensor to O_2 at elevated temperatures, sulphides can be recovered back to oxides as:

$$2CrS + 3O_2 \rightarrow 2CrO + 2SO_2 \quad (4)$$

$$2Cr_2S_3 + 9O_2 \rightarrow 2Cr_2O_3 + 6SO_2 \quad (5)$$

When oxygen is adsorbed on the chromium zone of strong localization at elevated temperatures, the potential between the WO_3 grains may be raised further and as a result the total resistance increases in comparison with the unmodified sample without any chromium. Abstraction of electrons from bulk WO_3 by the adsorbed oxygen results in the formation of surface states. When reducing gas like H_2S is adsorbed between the grains of WO_3, the potential barrier deceases as a result of oxidative conversion of the H_2S gas. H_2S reacts with adsorbed oxygen ions as:

$$H_2S + 3O^- \rightarrow H_2O + SO_2 + 3e^- \quad (6)$$

The amount of oxygen adsorbed on the surface of chrominated WO_3 film is more since chromium oxide forms misfit region between the grains of WO_3 and acts as efficient catalysts for oxygenation leading to unusual physical and chemical properties. For example, the adsorption energy can be higher for the misfit regions, and the discontinuity in the adsorption potential can give rise to unusual selectivity for WO_3 based semiconducting oxide sensors. More specifically, the electron-electron interaction in the presence of periodically, enhanced disorder can affect adsorbate-adsorbent interaction and the range of adsorbtion potentials leading to additional sensitivity improvement.

When the optimum amount of chromium oxide is incorporated on surface of the WO_3 film, chromium species would be distributed uniformly throughout the surface. This promotes catalytic reaction effectively leading to high initial conductivity of the film. This results into high gas response.

When the amount of chromium oxide on the surface of the film is less than the optimum, the surface dispersion is poor and amount is not sufficient to promote the reaction more effectively leading to decreased sensitivity. The maximum response to H_2S gas of chrominated WO_3 and unmodified WO_3 was observed at 250 ^{0}C and 350 ^{0}C respectively. This can be attributed to more oxygen deficiency as depicted by Fig. 8 and Fig. 9. The addition of Cr_2O_3 into WO_3 could change the grain size of WO_3 considerably and also change the catalytic property of WO_3.

TGA observations indicate that surface chrominated WO_3 is more stable than the pure WO_3. Therefore reproducibility of chrominated samples is expected to be more than pure WO_3. The oxygen adsorption mechanism of chrominated WO_3 is observed to be more effective as compared to the pure WO_3 leading to higher gas response.

Non-linear increase of conductivity of pure and chrominated WO_3 indicates semiconducting nature and is attributed to oxygen deficiencies in WO_3. The chromination of WO_3 enhance the electrical conductivity. This may be due to conducting nature of small particles of Cr_2O_3 segregated around the grain boundaries of WO_3,

Fast recovery and response to H_2S gas may be due to faster adsorption-desorption reaction on the surface of chrominated film. The large number of oxygen ion could adsorb on the misfit regions of chromium in absence of H_2S gas. These adsorbed oxygen ion could oxidize H_2S gas immediately on its exposure leading to the fast response and recovery of sensor.

6. Summary and Conclusions

1) Unmodified WO_3 thick films have different capability to recognize different gases at different operating temperatures. Therefore, it has poor selectivity.
2) Unmodified WO_3 thick films acts as a cigar smoke sensor at 300 ^oC, a H_2S sensor at 350 ^oC and an ethanol sensor at 400 ^oC.
3) Unmodified WO_3 thick films were surface activated (Cr_2O_3-modified) using dipping technique to enhance sensitivity and selectivity.
4) Unmodified and modified films showed decrease in conductivity with increase of temperature. Therefore they are NTC type materials.
5) The Cr_2O_3-modified WO_3 sensor (20 min) showed the selectivity to H_2S gas at 250 ^0C, suppressing the responses to other gases. Selectivity to H_2S gas for modified film is shifted from higher temperature 350 ^0C to lower temperature 250 ^0C.
6) Unmodified WO_3 film showed optimum response to H_2S gas at 520 ppm concentration at 350 ^0C. Initially response increases with the H_2S gas concentration, attains the maximum at 520 ppm concentration. The response decreases with further increase of gas concentration.
7) Modified WO_3 film showed optimum response to H_2S gas at 280 ppm concentration at 250^0C. Initially response increases with the H_2S gas concentration, attains the maximum at 280 ppm concentration. The response decreases with further increase of gas concentration.
8) Cr_2O_3-modified WO_3 (20 min) showed fast response (3 sec) and recovery time (7 sec) to H_2S gas at 250 ^0C
9) This study demonstrates the possibility of utilizing surface chrominated WO_3 thick film as a low cost sensor element for the detection of H_2S gas.

Acknowledgements

The author (RLP) sincerely thanks O.S.D and Director, BCUD, University of Pune for financial assistance to this research project. Author is very much thankful to Sarchitnis, N.D.M.V. Samaj, Nashik , Author is grateful to the Principal, K.T.H.M.College, Nashik for providing laboratory facilities and also thankful to the Head, Department of Physics, Arts, Science and commerce College, Nandgaon for his keen interest in this research project.

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