Heterostructured Ga_2O_3-Activated Bi_2O_3 Sensors for Chlorine Monitoring[1]

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ABSTRACT

The nanocrystalline Bi_2O_3 powder was synthesized by ultrasonicated microwave irradiation by employing centrifugation technique at all normal conditions. Fabrication of thick films of pure Bi_2O_3 powder was made by screen printing and firing at 400ºC for 30 min. Surface activations of the films involved the dipping of pure films into 0.01M aqueous solution of Gallium Nitrate for different intervals of time. The morphologies, surface topographies, constituents of elements present in the synthesized materials and crystallographic structures of the pure and surface activated films have been investigated by XRD, FE-SEM, E-DAX, etc. It has been investigated that, the Ga_2O_3 activated Bi_2O_3 (30 min) sample exhibits crucial response to 20 ppm Cl_2 gas at 250ºC. Electrical and gas monitoring performance of thick films of pure and activated Bi_2O_3 have been studied and discussed.

Keywords: *Heterostructure, Nanocrystalline Bi_2O_3, Ga_2O_3, Thick films, Cl_2 Sensor*

1. Introduction

The research and development in the gas sensing field have emerges the new challenges for the researchers, scientists and industrialists. Hence, there is a great scope of innovations for this material to fabricate gas sensors [1]. Metal oxides such as Ga_2O_3, ZnO, SnO_2, WO_3, CuO, ZrO_2, etc. have attracted great deal of interest as their electrical and optical characteristics get changes on the exposure of reducing or oxidizing gases [2-8]. Metal oxide thick films offer good possibilities in tailoring the gas response and selective nature of the gas sensors, by changing the various parameters. Gallium oxide (Ga_2O_3) is a versatile wide band gap semiconducting metal oxide with wide applications such as transparent conducting electrodes, phosphors, dielectric gates, gas sensors, etc. [9]. Ga_2O_3 is very promising materials in oxygen sensing, but at high temperatures from 600-1000ºC which is not desirable [10-11].

Water disinfection processes, paper and pulp industries, drinking and wastewater treatment plants, bleaching processes, etc. use chlorine widely. Long and continuous exposure to chlorine can be detrimental for humans [12-14]. Chlorine has excellent bleaching ability, but once it is discharged in aquatic systems, it interacts with other industrial effluents to produce a host of chlorinated organic such as dioxin. Dioxin persists in the environment for prolonged periods and has a tendency to bio-accumulate in the food chains, which elicit toxic effects to humans, viz. skin infection, psychological disorders and even liver damage. Gas chromatography, chemical detecting tubes and electrochemical sensing techniques are available for the detection of chlorine gas in the environment, but they are inconvenient techniques to monitor chlorine gas at low temperature [15-18]. It is therefore, necessary to monitor chlorine gas and to develop the efficient chlorine gas sensors.

2. Materials and Methods

2.1 Synthesis of Nanocrystalline Bi_2O_3

Nanocrystalline Bi_2O_3 powder was synthesized by ultrasonicated microwave irradiation by employing centrifugation technique at normal conditions. For the

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synthesis, 0.05 M aqueous solution of bismuth nitrate pentahydrate was prepared and ammonium hydroxide was added drop wise slowly with the constant stirring on hot plate, till ppt forms and pH reaches at 11. The ppt was washed 5 times with distilled water. The washed ppt was allowed to ultrasonication for 30 minutes and microwave irradiation and centrifugation. The collected ppt was calcined at 400°C for 2 hrs.

2.2 Thick Film Fabrication

Thixotropic paste of the synthesized powder was formulated by mixing the nanostructured powder of pure Bi_2O_3 with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and turpineol. The ratio of inorganic to organic part was kept as 80:20 in formulating the thixotropic pastes. The thixotropic pastes were screen printed on the glass substrates in the desired patterns. Films prepared were dried at 80°C under an IR lamp, and fired at 400°C for 30 min in air ambient.

2.3 Surface Activation of Thick Films

Surface activation of thick films of pure Bi_2O_3 was achieved by dipping them into a 0.01 M aqueous solution of gallium nitrate for different intervals of time viz. 5 min, 15 min, 30 min and 45 min and dried at 80°C under an IR lamp, and fired in muffle furnace at 400°C for 30 min in air ambient. The particles of gallium nitrate dispersed on the film surface would be transformed to gallium oxide (Ga_2O_3) during firing process. Thus, the sensor elements with different mass % of Ga_2O_3 incorporated in to thick films of pure Bi_2O_3 were obtained. Silver contacts were made by vacuum evaporation for electrical measurements and the chlorine gas sensing performance.

3. Results and Discussions

3.1 Material Characterizations

3.1.1 Structural Properties (X-Ray Diffraction Studies)

3.1.2 Energy Dispersive Analysis by X-Rays (E-DAX)

The mass % of Bi and O in each samples (Table 1) are not as per the stoichiometric proportion and the material is having semiconducting nature. It is cleared from Table 1 that the mass % of Ga_2O_3 (Bi_2O_3) goes on increasing (decreasing) with activation time.

3.1.3 Microstructural Analysis (SEM)

Figs. 2 (a-d) depict the microstructures of Ga_2O_3 activated Bi_2O_3 thick films for various activation times, viz. 5 min, 15 min, 30 min and 45 min. It was observed that, the Ga_2O_3 particles are distributed on the surface of Bi_2O_3 thick films. The figures depict the physisorption of

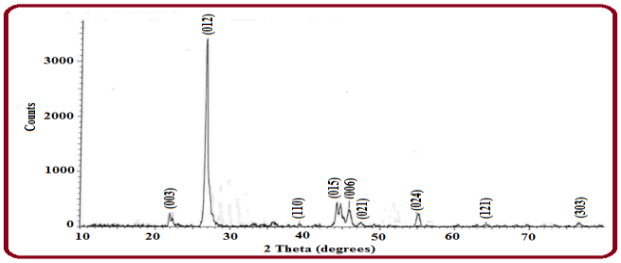


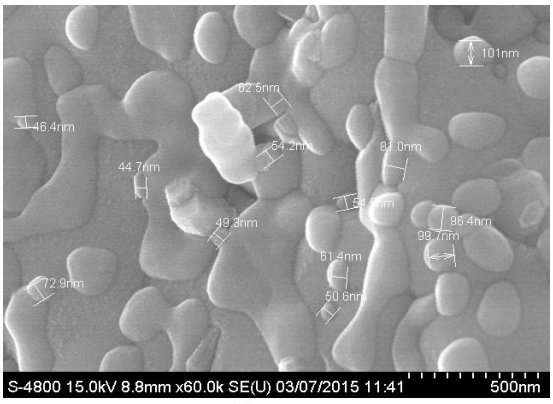
Fig. 1: XRD pattern of pure Bi_2O_3 powder

X ray diffraction studies of pure Bi_2O_3 powder was carried out using BRUKER AXSD8 (Germany) advance model X ray diffraction with $CuK\alpha_1$ (λ=1.54056 Å) radiation in the 2θ range 20°-80°. The scanning speed of the specimen was maintained 0.5° / min. Fig. 1 depicts the XRD pattern of pure Bi_2O_3 powder. The average crystallite size for this sample was determined using Scherer's formula and was observed to be 22.6 nm. Observed peaks match well with JCPDS data of Bi_2O_3. It was also observed from XRD analysis that, as very minute quantity of activator Ga_2O_3 was dispersed on the surface of the films and few incorporated inside the bulk of the films of Bi_2O_3, hence, it doesn't appear in the XRD patterns of the activated films. Almost, all the XRD patterns of the activated films are nearly same. So, these XRD patterns are not given here.

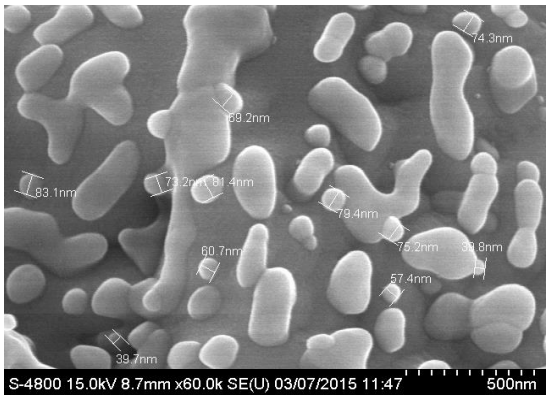
Table 1: Elemental analysis of pure and Ga_2O_3 activated Bi_2O_3 thick films

Mass %	Activation Time (min)					
	0 (Pure) (Expected)	0 (Pure) (Observed)	5	15	30	45
Bi	89.70	91.34	72.51	68.13	59.45	50.57
O	10.30	08.66	02.71	01.41	03.94	07.00
Bi_2O_3	100	100	66.69	59.05	50.77	42.96
Ga	0.00	0.00	24.78	30.46	36.62	42.43
Ga_2O_3	0.00	0.00	33.31	40.95	49.23	57.04
Ga_2O_3-Bi_2O_3	100	100	100	100	100	100

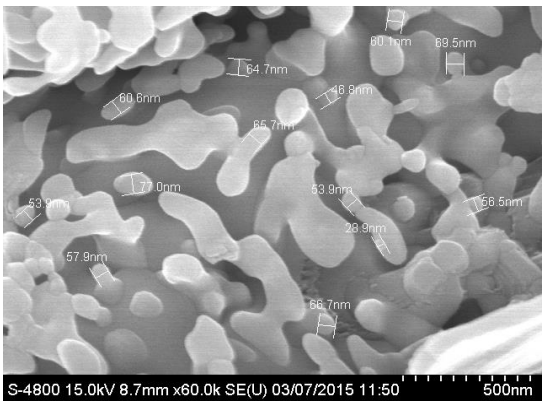
Ga_2O_3 grains on the Bi_2O_3 grains of the film surface, as islands.



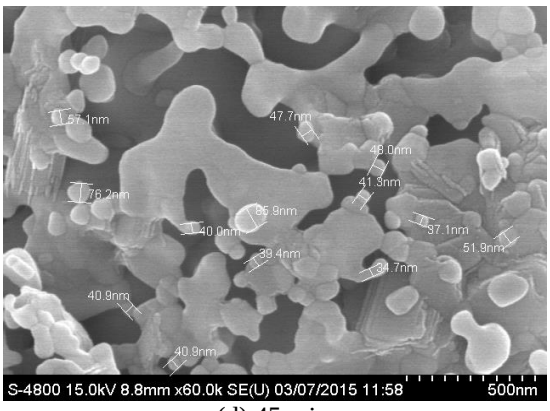
(a) 5 min



(b) 15 min



(c) 30 min



(d) 45 min

Fig. 2: Micrographs of Ga_2O_3 activated Bi_2O_3 films for (a) 5 min, (b) 15 min, (c) 30 min and (d) 45 min

The average size of Ga_2O_3 grains on film surface is in the range from 30 nm to 100 nm. The films consist of voids and continuous distribution of the Ga_2O_3 grains on the film surface. Thick film of Ga_2O_3 activated Bi_2O_3 (30 min) was observed to be most sensitive to 20 ppm Cl_2 at 250°C. The high performance of this film in Cl_2 gas sensing may be attributed to the fabrication of nanorods on the film surface and intergrain boundaries of Ga_2O_3 - Bi_2O_3 developed on the film surface, which modifies the energy levels producing the large number of surface active sites. So, the large surface active sites are made available to reach the gas molecules to the intergrain boundaries, enhancing Cl_2 sensing.

3.2 I-V Characteristics of Sensor

3.2.1 I-V Characteristics

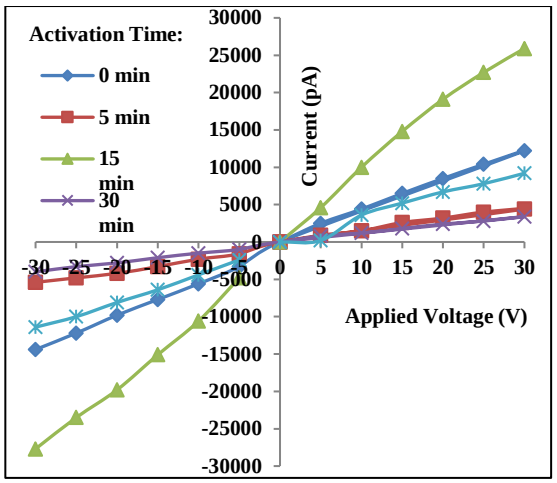


Fig. 3: I-V characteristics of Ga_2O_3 activated Bi_2O_3 thick films

The symmetrical I-V characteristics of pure and Ga_2O_3 activated Bi_2O_3 thick films in Fig. 3 confirms the ohmic natures of materials as well as silver contacts made on the films. The material is therefore said to have the resistive properties.

3.2.2 Electrical Conductivity

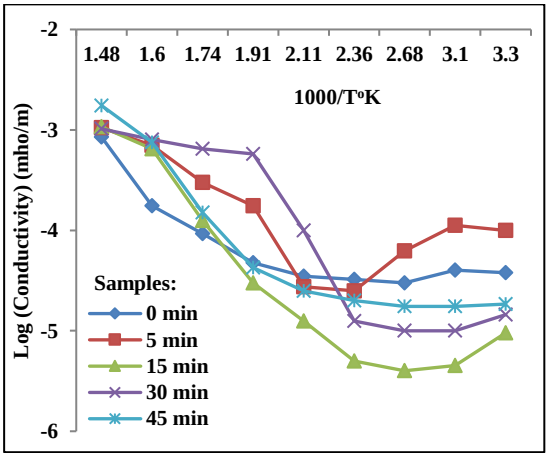


Fig. 4: Conductivity-temperature profile of Ga_2O_3 activated Bi_2O_3 films

Fig. 4 depicts the variation of logarithm of electrical conductivity with the reciprocal of operating temperature for Ga_2O_3 activated Bi_2O_3 thick films. The conductivities of all samples increased with increase in operating temperature (above 200°C), which could be attributed to negative temperature coefficient of resistance and the semiconducting nature of the Ga_2O_3 activated Bi_2O_3 thick films. Below 200°C temperature, the conductivities nearly remain same, exhibiting the resistive nature of the materials.

3.3 Gas Sensing Performance

3.3.1 Temperature Based Gas Sensing Performance of Pure Bi2O3

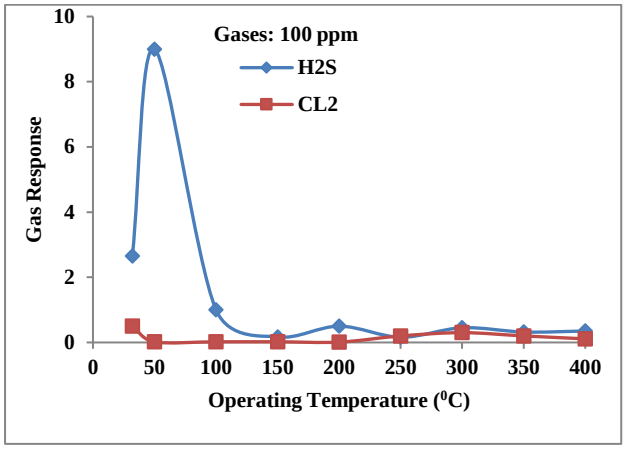
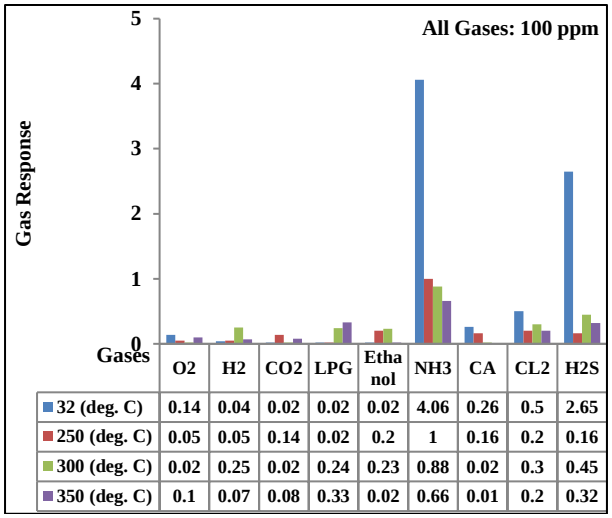


Fig. 5: Variation of H_2S and Cl_2 response of pure Bi_2O_3 thick film with operating temperature (^oC)

The gas response of pure Bi_2O_3 thick films to 100 ppm H_2S and Cl_2 gases as a function of operating temperature is indicated in Fig. 5. It is observed from Fig. 5 that, the pure Bi_2O_3 thick film is almost insensitive to Cl_2 at all temperature range i. e. from room temperature to 400^{o}C. The film responds (though less) to H_2S at room temperature (32^{o}C) as well as at 50^{o}C.

3.3.2. Gaseous Species Based Performance of Pure Bi2O3



Gases	O2	H2	CO2	LPG	Ethanol	NH3	CA	CL2	H2S
32 (deg. C)	0.14	0.04	0.02	0.02	0.02	4.06	0.26	0.5	2.65
250 (deg. C)	0.05	0.05	0.14	0.02	0.2	1	0.16	0.2	0.16
300 (deg. C)	0.02	0.25	0.02	0.24	0.23	0.88	0.02	0.3	0.45
350 (deg. C)	0.1	0.07	0.08	0.33	0.02	0.66	0.01	0.2	0.32

Fig. 6: Selectivity of pure Bi_2O_3 to NH_3 and H_2S gases

It is cleared from Fig. 6 that, pure Bi_2O_3 thick film sensor showed selective response to 100 ppm NH_3 gas at room temperature (32^{o}C), among the various gases, viz. O_2, H_2, CO_2, LPG, ethanol, capronaldehyde (CA) and Cl_2. Poor selectivity and less response are the major drawbacks of pure Bi_2O_3 thick films in gas sensing applications.

3.3.3 Temperature Based Gas Sensing Performance of Activated Bi2O3

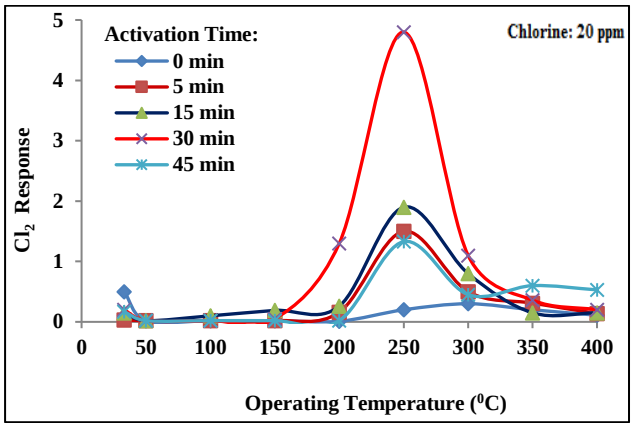


Fig. 7: Variation of Cl_2 response with operating temperature of Ga_2O_3 activated Bi_2O_3 thick films

Fig. 7 depicts the variation of Cl_2 gas response of surface activated Bi_2O_3 thick films by Ga_2O_3 to 20 ppm Cl_2 as a function of operating temperature. The surface activated Bi_2O_3 thick film (30 min) was observed to be most sensitive to Cl_2 at 250^{o}C. The Cl_2 response increases with operating temperature, reaches maximum at 250^{o}C and decreases with further increase in operating temperature.

3.3.4 Chlorine Concentration Based Performance of Activated Bi_2O_3

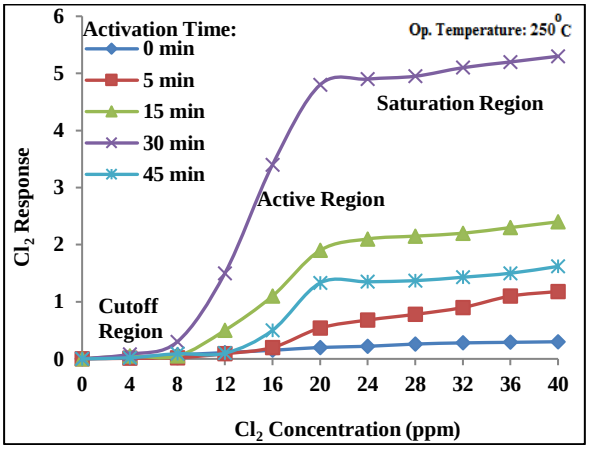


Fig. 8: Variation in Cl_2 response with Cl_2 gas concentration (ppm)

The variation of Cl_2 response of activated films as a function of Cl_2 gas concentration at 250^{o}C temperature has been depicted in Fig. 8. Among all, 30 min activated film was observed to be most sensitive to 20 ppm Cl_2 at 250^{o}C. The responses were observed to increase linearly with increasing gas concentration up to 20 ppm at 250^{o}C. The rate of increase in response was relatively larger up to 20 ppm and saturated beyond 20 ppm. Thus, the active region of the sensor would be from 4 ppm up to 20 ppm. At 20 ppm gas concentrations, the unimolecular layer of gas molecules would be expected to form on the surface of the sensor which would interact with the surface more actively giving proportional response. There would be the formation of multilayer of gas molecules on the sensor

surface at the higher gas concentrations resulting in saturation in response beyond 20 ppm gas. For proper functioning, the sensor should work in the active region.

3.3.5 Surface Activation Based Performance

The response of activated films to Cl_2 as a function of the activation time is shown in Fig. 9. The film activated for 30 min was observed to be the most sensitive to Cl_2 among all other tested gases. It showed the highest response of the order of 4.8 to 30 min activated sample to 20 ppm Cl_2 gas at 250ºC and lower to the rest of activated samples of different activation time interval. The crucial response of this sensor to Cl_2 gas may be attributed to the fabrication of nanorods on the film surface and heterostructured intergrain boundaries of Ga_2O_3 - Bi_2O_3 developed on the film surface, which modifies the energy levels producing the large number of surface active sites.

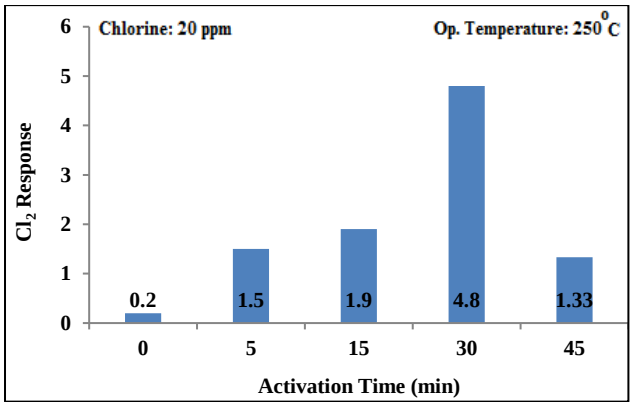
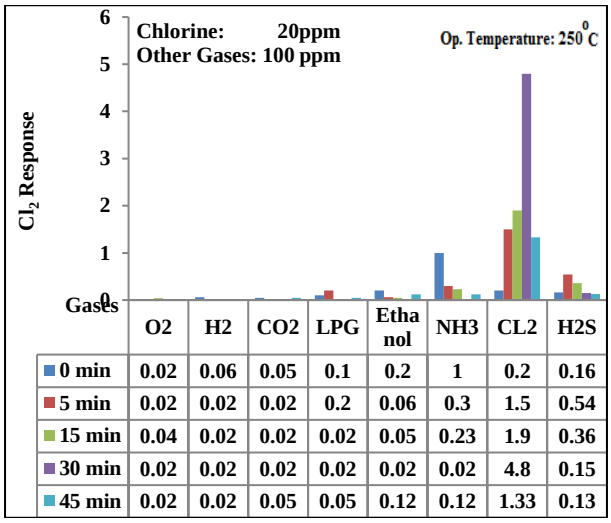


Fig. 9: Variation of Cl_2 response with activation time

3.3.6 Gaseous Species Based Performance of Activated Bi2O3



Gases	O2	H2	CO2	LPG	Ethanol	NH3	CL2	H2S
0 min	0.02	0.06	0.05	0.1	0.2	1	0.2	0.16
5 min	0.02	0.02	0.02	0.2	0.06	0.3	1.5	0.54
15 min	0.04	0.02	0.02	0.02	0.05	0.23	1.9	0.36
30 min	0.02	0.02	0.02	0.02	0.02	0.02	4.8	0.15
45 min	0.02	0.02	0.05	0.05	0.12	0.12	1.33	0.13

Fig. 10: Selectivity of Ga_2O_3 activated Bi_2O_3 thick films to Cl_2 gas among different gases

Fig. 10 depicts the selectivity of Ga_2O_3 activated Bi_2O_3 thick film sensors to 20 ppm Cl_2 at 250ºC temperature. The Ga_2O_3 activated Bi_2O_3 (30 min) sensor showed high selectivity to Cl_2 and could distinguish the Cl_2 among all the gases such as: O_2, H_2, CO_2, LPG, ethanol, NH_3 and H_2S.

3.3.7 Response – Recovery Performance of Activated Bi2O3

The response and recovery of the Ga_2O_3 activated Bi_2O_3 thick film sensor is represented in Fig. 11. The response was quick (~ 8 s) to 20 ppm Cl_2, while the recovery was fast (~10 s). The negligible quantity of the surface reaction product and its high volatility explains its quick response to Cl_2 and fast recovery to its initial chemical status.

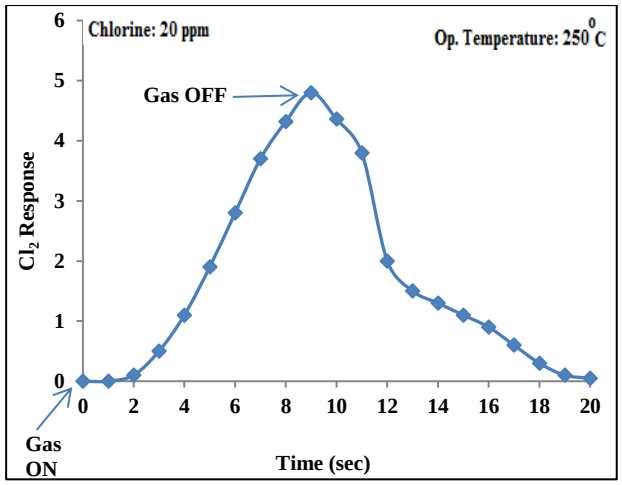


Fig. 11: Response and recovery of Ga_2O_3 activated Bi_2O_3 sensor

4. Chlorine Gas Sensing Mechanism of Activated Bi_2O_3

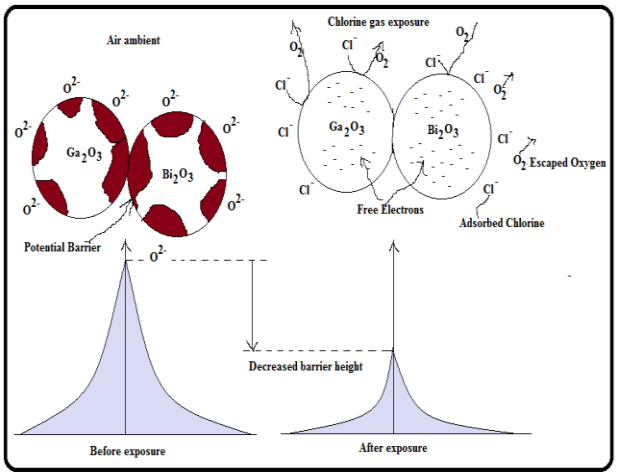


Fig. 12: Chlorine sensing mechanism

Gas sensing phenomenon is the surface phenomenon. So, the exposure of gas on the surface of the sensor can lead the change of surface resistance, instead of change of bulk resistance [19]. Upon exposure of chlorine gas, the interaction of chlorine molecules with surface of Ga_2O_3 activated Bi_2O_3 thick film causes the transfer of electrons between semiconducting surface and adsorbates. Adsorption of atmospheric oxygen molecules decreases the electronic conductivity of the material of the film, as described in (1) [20-23].

$$O_{2\,(air)} + 2e^- \rightarrow 2O^-_{(film\ surface)} \quad \ldots\ldots\ldots 1$$

The mass % of Bi and O in each sample are not as per the stoichiometric proportion and all samples were observed to be the excess in oxygen and deficient in bismuth. However, 15 min activated sample, alone, was observed to be oxygen deficient, as indicated in Table 1. Therefore, maximum numbers of free electrons are available in this film. This enhances the n-typeness of the film. Upon exposure, chlorine molecules replace the adsorbed oxygen, donating free electrons to the material of the film (Fig. 12). The reaction in (2) is responsible for chlorine sensing [16].

$$Cl_{2\,(gas)} + O_{2(ad)}{}^{2-} \rightarrow 2\,Cl_{(ad)}{}^- + O_{2\,(gas)} + 2\,e^-_{(cond.band)} \quad \ldots.2$$

From Fig. 12, it is cleared that, each adsorbed oxygen molecules captured two electrons, and each adsorbed oxygen molecules are replaced by Cl_2 molecules capturing only one electron and making free electrons as shown in (2). Thus the numbers of free electrons in the conduction band of the material increases, enhancing the chlorine response at high temperature (250^{o}C).

5. Conclusions

From the results obtained, following conclusions can be made for Cl_2 sensing performance of the sensor.

1. Pure bismuth oxide was almost insensitive to Cl_2 traces at all temperature range.
2. Surface activation by dipping process is one of the most suitable methods of modifying the surface of thick films.
3. Ga_2O_3 activated Bi_2O_3 (30 min) thick film has good sensitivity and selectivity to 20 ppm Cl_2 at 250^{o}C.
4. Ga_2O_3 as an additive in Bi_2O_3 is outstanding in promoting the Cl_2 sensing.
5. The sensor showed very rapid response and recovery to Cl_2 gas.

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