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TEMPERATURE DEPENDENCE OF GAS SENSITIVITY OF FERRIC OXIDE THIN FILMS IN CO_2 GAS, ACETONE, ETHANOL AND METHANOL VAPORS

P. Samarasekara [1], M.S.P.K. Gunasinghe [1], P.G.D.C.K. Karunarathna [2], H.T.D.S. Madusanka [2] and C.A.N. Fernando [2]

[1]Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka

[2]Department of Nano Science Technology, Wayamba University of Sri Lanka, Kuliyapitiya, Sri Lanka

Abstract

Thin films of ferric oxide ($\alpha-Fe_2O_3$) were synthesized by the doctor blade method starting from a solution of iron acetate and PEG binder. The samples were subsequently annealed at 500 ^0C in air for one hour. The surface morphology of the samples was determined by SEM. The samples are consists of closely packed spherical particles in the size of about 150 nm. The gas sensitivity, recovery time and response time of the $\alpha-Fe_2O_3$ samples were measured in CO_2 gas, acetone, ethanol and methanol vapors at room temperature. Then the same parameters of the $\alpha-Fe_2O_3$ samples in CO_2 gas were measured at different operating temperatures from the room temperature to 200 ^0C. The $\alpha-Fe_2O_3$ samples indicated the highest sensitivity of 66.91% in CO_2 gas at the room temperature compared with the other three vapors. This is one of the highest gas sensitivities reported for the $\alpha-Fe_2O_3$ thin films in CO_2 gas. However, the best recovery and response times of the samples were found in the ethanol vapor at the room temperature. The gas sensitivity of the samples in CO_2 gas increased with the operating temperature up to 170 ^0C, and then gradually decreased with the operating temperature. The gas sensitivity of $\alpha-Fe_2O_3$ samples in CO_2 gas increases by a factor of 1.17 at 170 ^0C, compared with the gas sensitivity in CO_2 gas at the room temperature. In addition, the best respond and recovery times in CO_2 gas were observed at 170 ^0C.

Keywords: *Doctor blade method, gas sensors, gas sensitivity, operating temperature*

1. Introduction:

Iron oxides have different stoichiometrics such as FeO, Fe_2O_3 and Fe_3O_4. Iron oxide finds potential applications in photodynamic therapy, agriculture applications, magnetic recording, magnetic memory devices, gas sensors and biosensors. Thin films of γ–Fe_2O_3 have been synthesized on glass substrates at 350 ^0C, and thin films of α–Fe_2O_3 have been deposited between 400 and 500 ^0C by gas phase deposition [1]. Thin films of iron oxide have been fabricated by both post-oxidation of pure Fe ultra-thin films and by evaporating Fe onto the MO substrates [2]. Colored iron oxide thin films have been grown by Sol-gel technique [3]. Iron oxide thin films have been synthesized on fused quartz substrate using simple metal organic deposition from Fe-(III) acetylacetonate as the organic precursor [4]. Fe_3O_4 thin films have been sputtered using a target consisting of a mixture of Fe_3O_4 and Fe_2O_3 onto Si and glass substrates [5]. Also thin films of hematite have been synthesized using pulsed laser depositions (PLD) [6]. Fe_2O_3 thin film gas sensor sensitive to organic vapors and hydrogen gas have been synthesized using cathodic sputtering [7]. Fe_2O_3 gas sensing films have been fabricated by normal pressure chemical vapor deposition to detect acetone and alcohol [8]. Fe_2O_3 thick film sensors have been applied to detect CH_4, H_2 and NH_3 [9]. Hollow balls of nano Fe_2O_3 have been employed to detect dimethyl methylphosphonate at room temperature [10]. It is possible to control the gas sensing properties of hematite nanocrystals by controlling the

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morphology [11]. Gas sensing properties of p-type α–Fe_2O_3 polyhedral particles have been investigated [12]. $NaBH_4$ added α–Fe_2O_3 microparticles with size of 1-10 μm have been prepared [13].
Thin films have been synthesized using chemical vapor deposition, sputtering techniques and evaporation techniques incorporated with vacuum previously [14, 15, 16, 17]. Compared to the expensive techniques with vacuum, doctor blade method was found to be lower in cost and faster. The band gap of semiconductor particles can be determined using electrical conductivity measurements too [18]. Iron oxide belongs to the category of ferrimagnetic materials. Magnetic properties of ferromagnetic and ferrite thin films have been investigated using the second and third order perturbed Heisenberg Hamiltonian by us [19-23]. Applications of gas sensors have been presented in many manuscripts [24-31]. In this manuscript, we report the gas sensing properties of α–Fe_2O_3 thin films in CO_2 gas and many vapors at different operating temperatures.

2. Experimental:

Initially 1.5002 g of iron acetate nanoparticles was dissolved in 10 ml of water to prepare a solution of 2 M. Then the solution was stirred on a magnetic stirrer at 600 rpm for 1 hour to mix the solution. The solution was placed inside a furnace at 500 ^{0}C for two hours with 10 ^{0}C min^{-1} heating rate. Then 0.0503 g of polyethylene glycol (PEG) was mixed with 8 ml of water. It was placed on a magnetic stirrer and stirred at 45 ^{0}C temperature for 15 minutes. Thereafter, PEG solution (2 ml) was added to iron acetate solution, and a few drops of ethanol was added to it. Then the solution was placed on the magnetic stirrer, and it was stirred at 600 rpm for two hours at 50 ^{0}C temperature. Finally the prepared iron acetate-PEG solution was applied to a conductive FTO glass plate or a normal non-conductive glass plate to prepare α–Fe_2O_3 thin films using a doctor blade method. Thin films grown on conductive FTO glass plates were used for gas sensitivity measurements. FTO glass plates with the area of 3.5 cm x 2 cm were used. A strip of 0.6 cm x 2 cm was scratched in the middle of the conducting side on FTO. Then glass slides were well cleaned using ethanol. Because the scratched glass slide is used to fabricate the gas sensor, only the α–Fe_2O_3 layer conducts the electric current. In the doctor blade method, cello tapes glued to the edges of the glass plates were used to control the thickness. First the prepared samples were heated on hot plate at 50 ^{0}C temperature for 1 hour. Then the thin films were cooled down in normal air for 2 hours. Thereafter, they were placed inside the oven at 150 ^{0}C temperature for 1 hour to remove excess oxygen and water vapor from the sample. Next the thin films were annealed in the furnace at 500 ^{0}C for one hour in air to crystallize the phase of α–Fe_2O_3
α–Fe_2O_3 thin films were connected to a 5 V power supply for 6 hours to stabilize the sensor. Gold coated electrodes and wires were used for all the connections. The sensor electrode wires were connected to a Keithley 6400 source meter unit to measure the current carrying through the gas sensor. Then the Keithley 6400 source meter was adjusted for current measuring mode, and 5.0 V was applied to the gas sensor. Next the measured time period was adjusted to 5000 s, and "AUTO LAB" measuring unit was switched on to measure the current carrying through the gas sensor. After stabilizing the current, some known amount of CO_2 gas (1000 ppm) was injected in to the glass chamber using a syringe. Then electric current increased and reached the saturated value of the current, and this saturated current was noted down. The time taken to reach the saturated current was also measured. This is called the respond time. Thereafter, normal atmospheric air was pumped in to the glass chamber to remove the CO_2 gas, and the air was pumped continuously in to the glass chamber until the current reading returned to initial stable value. The time taken to reach the initial stable value was also measured. This is called the recovery time. Then the air pump was switched off and, few minutes were given to stabilize the gas sensor. Thereafter, CO_2 gas was introduced again to the gas chamber, and above procedure was repeated to obtain another current variation cycle. This procedure was repeated for the gas sensors prepared with the binder (PEG), and the current response variation was compared. The same procedure was repeated to measure gas sensitivity of iron oxide thin films in methanol, ethanol and acetone vapors.

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The gas sensitivity was measured at different operating temperatures as follows. The room temperature was found using a thermocouple connected to the gas sensor. Then the gas sensor was heated to temperature of 60 ^{0}C using a coil heater connected to a power supply. Few minutes were given to stabilize the initial current. Then above procedure was repeated to measure the gas sensitivity in different gases and vapors. Similarly the gas sensitivity, recovery time and response time were measured at operating temperatures of 90, 120, 150, 180 and 210 ^{0}C. Surface morphology and particle size were determined using Zeiss Evols 15 scanning electron microscope (SEM).

3. Results and Discussion:

All the samples described in this section were prepared with PEG binder by the doctor blade method. The samples were subsequently annealed at 500 ^{0}C for one hour in air to crystallize the single phase of $\alpha-Fe_2O_3$. According to the XRD, FTIR and UV-visible data, the single phase of $\alpha-Fe_2O_3$ could be crystallized under these conditions [32]. Figure 1 shows the SEM micrograph of the $\alpha-Fe_2O_3$ thin films sample. Fe_2O_3 spherical shape particles can be observed. Particles are closely packed without any voids. The sample seems to be uniform. Therefore, SEM image observation reveals that prepared $\alpha-Fe_2O_3$ products consists of spherical grains with diameter around 150 nm.

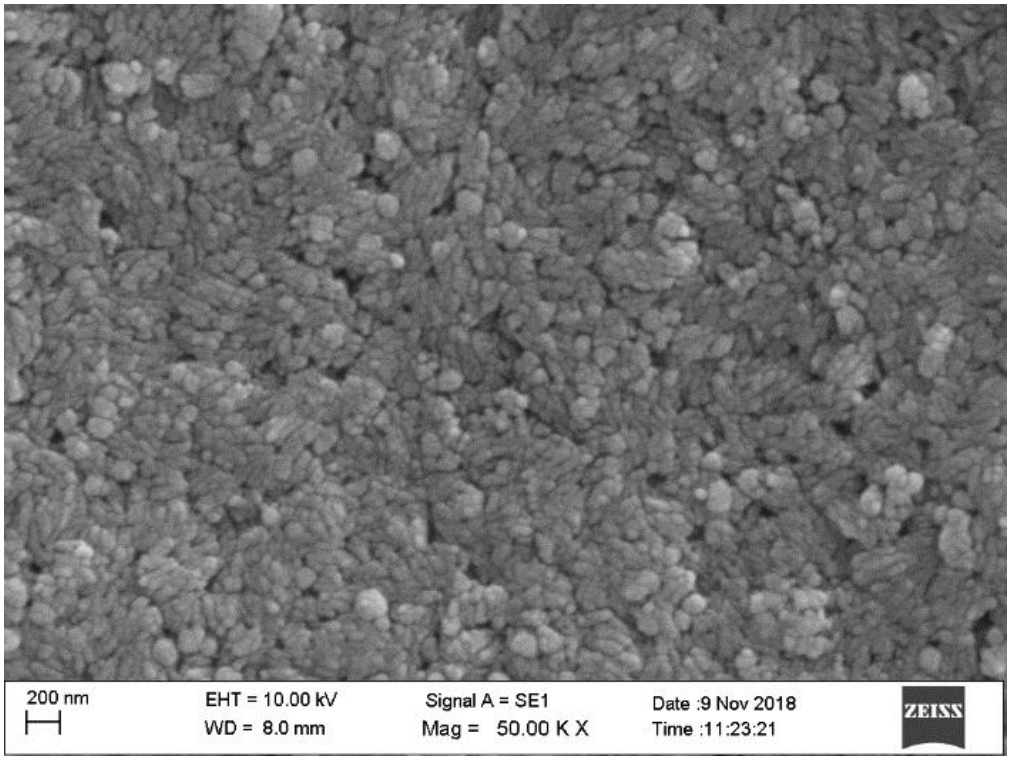

Figure 1: SEM image of the $\alpha-Fe_2O_3$ thin film prepared by the doctor blade method.

Figure 2 represents the curves of current, resistance and gas sensitivity versus time for CO_2 gas, acetone, ethanol and methanol vapors at the room temperature (28 ^{0}C). The current (I) in μA range was measured by AUTO LAB unit. Because 5V is applied to the sample, the resistance was calculated using R=5/I. The gas sensitivity of $\alpha-Fe_2O_3$ was measured at 1000 ppm gas or vapor amount in the gas chamber. The gas sensitivity was calculated using the following equation.

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$$\text{Gas sensitivity } = \frac{\left|R_g - R_a\right|}{R_a} \times 100\%$$

Here R_g is the saturated value of the resistance of the sample after the gas is completely absorbed by the sample, and R_a is the saturated value of the resistance after the gas is completely released by the sample.

According to the curves, CO_2 gas indicates the maximum gas sensitivity of 66.91% at the room temperature. The response and recovery times of $\alpha - Fe_2O_3$ thin film in CO_2 gas are 819 and 619 s, respectively. Gas sensitivity of $\alpha - Fe_2O_3$ thin film in acetone vapor is 56.43%, and response and recovery times are 310 and 344 s, respectively. For ethanol vapor, the gas sensitivity is 38.27%, and response and recovery times are 69 and 86 s, respectively. The lowest gas sensitivity at room temperature was observed in methanol vapor, and it is 32.04%. The response and recovery times in methanol vapor are 665 and 494 s, respectively. CO_2 gas takes the maximum time to respond to the gas sensor. In the presence of ethanol vapor, $\alpha - Fe_2O_3$ gas sensor responses quickly. But the gas sensitivity value is low in ethanol vapor. According to the gas sensitivity measurements, $\alpha - Fe_2O_3$ gas sensor can be used to detect CO_2 gas, acetone, ethanol and methanol vapors, however, it is more suitable to detect CO_2 gas.

The resistance of $\alpha - Fe_2O_3$ thin film decreases after absorbing CO_2 gas, acetone and ethanol vapors. However, the resistance of $\alpha - Fe_2O_3$ thin film increases after absorbing methanol vapor. This is related to the chemisorption and physisorption processes. Chemisorption is a kind of adsorption which involves a chemical reaction between the surface and the adsorbate. New chemical bonds are generated at the adsorbent surface. Physisorption is the physical bonding of
gas molecules to the surface of a solid or liquid that the gas comes into contact with at low temperatures. This occurs due to Van der Waals forces.

Atmospheric O_2 molecules are physiosorbed on the surface site, and become ionized by taking an electron from the conduction band as following. This leads to an increase in resistance of the sensor material.

$$O_2 + 2e^- \rightarrow 2O^-$$

The reducing gas (R) reacts with the chemisorbed oxygen, thereby releasing an electron back to the conduction band and decreasing the resistance of the sensor material as following.

$$R + O^- \rightarrow RO + e^-$$

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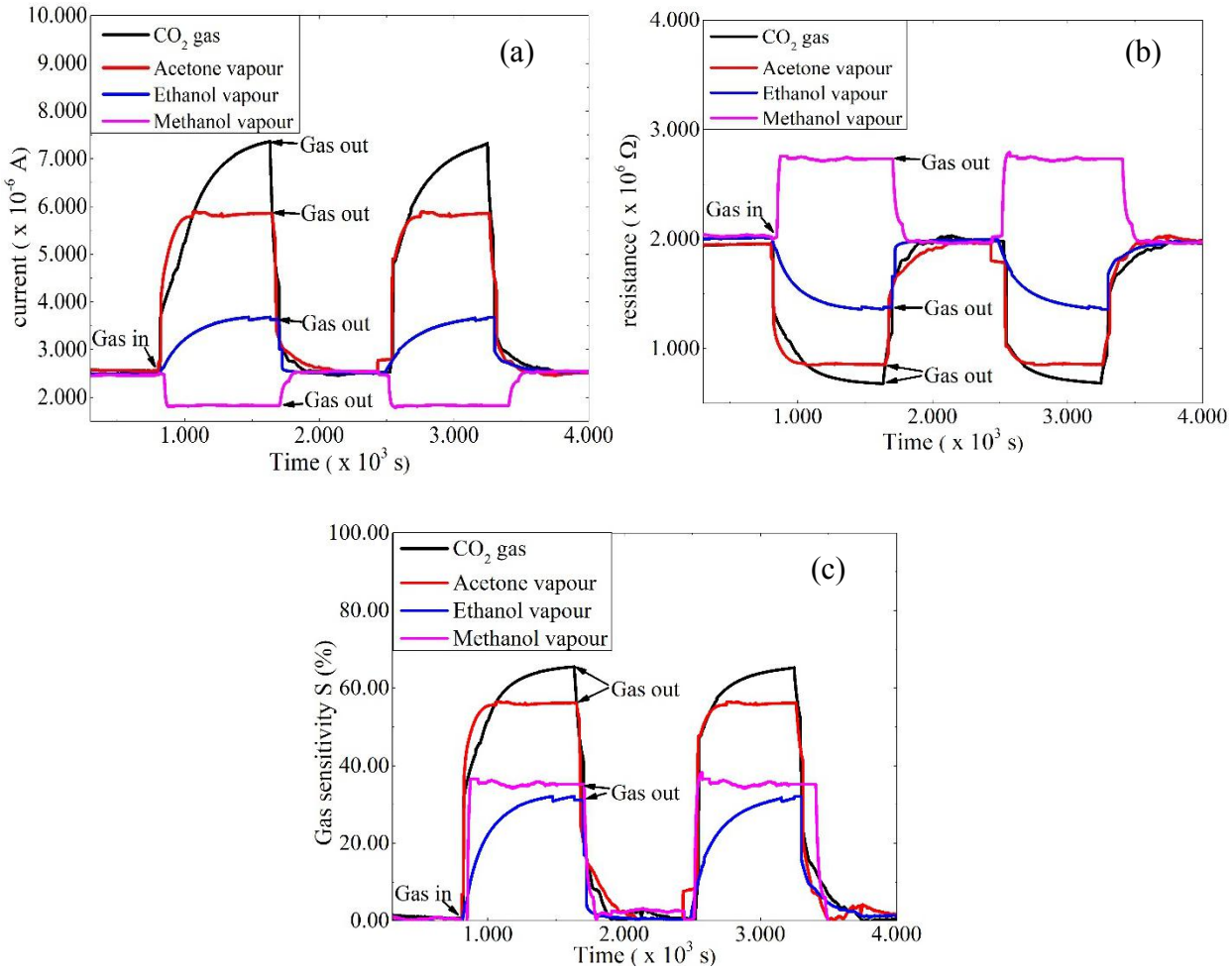

Figure 2: Graphs of current, resistance and gas sensitivity versus time for CO_2 gas, acetone, ethanol and methanol vapors.

Figure 3 shows the bar chart of the gas sensitivity for CO_2 gas, acetone, ethanol and methanol vapors at the room temperature. Table 1 represents the response time, recovery time and the gas sensitivity for CO_2 gas, acetone, ethanol and methanol vapors at the room temperature.

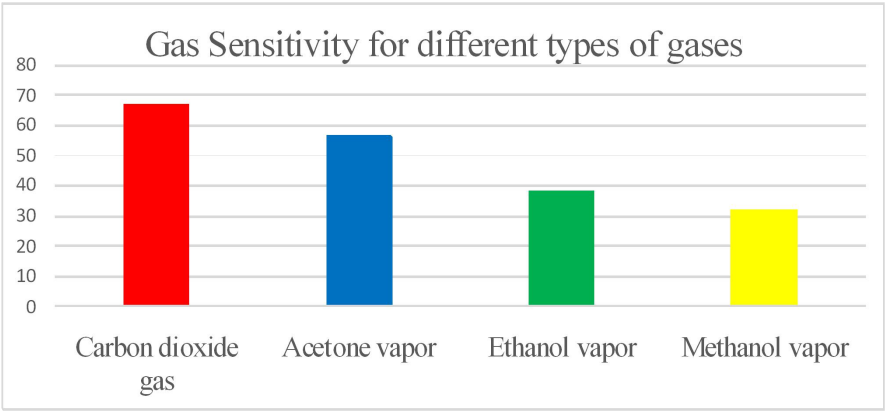

Figure 3: Bar chart of the gas sensitivity for CO_2 gas, acetone, ethanol and methanol vapors.

Table1: Response time, recovery time and the gas sensitivity for CO_2 gas, acetone, ethanol and methanol vapors.

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Gas type	Response time (s)	Recovery time (s)	Gas sensitivity (%)
Carbon dioxide gas	819	619	66.91
Acetone vapor	310	344	56.43
Ethanol vapor	69	86	38.27
Methanol vapor	665	494	32.04

Figure 4 shows the variation of the current, resistance and gas sensitivity with time for 1000ppm of CO_2 gas at different temperatures. At room temperature, the gas sensitivity of CO_2 in $\alpha-Fe_2O_3$ gas sensor is 66.91%. When the temperature of the gas sensor is increased, kinetic energy of atoms increases. At high kinetic energy, more electrons are excited into the conduction band, and electron density of the gas sensor becomes high. Electric field applied to the gas sensor increases the mobility of the electrons at high temperatures, and the electric current of the gas sensor increases up to a certain temperature. After a certain temperature, the collisions between conduction electrons dominate. As a result, the electric current decreases with the temperature after a particular temperature.

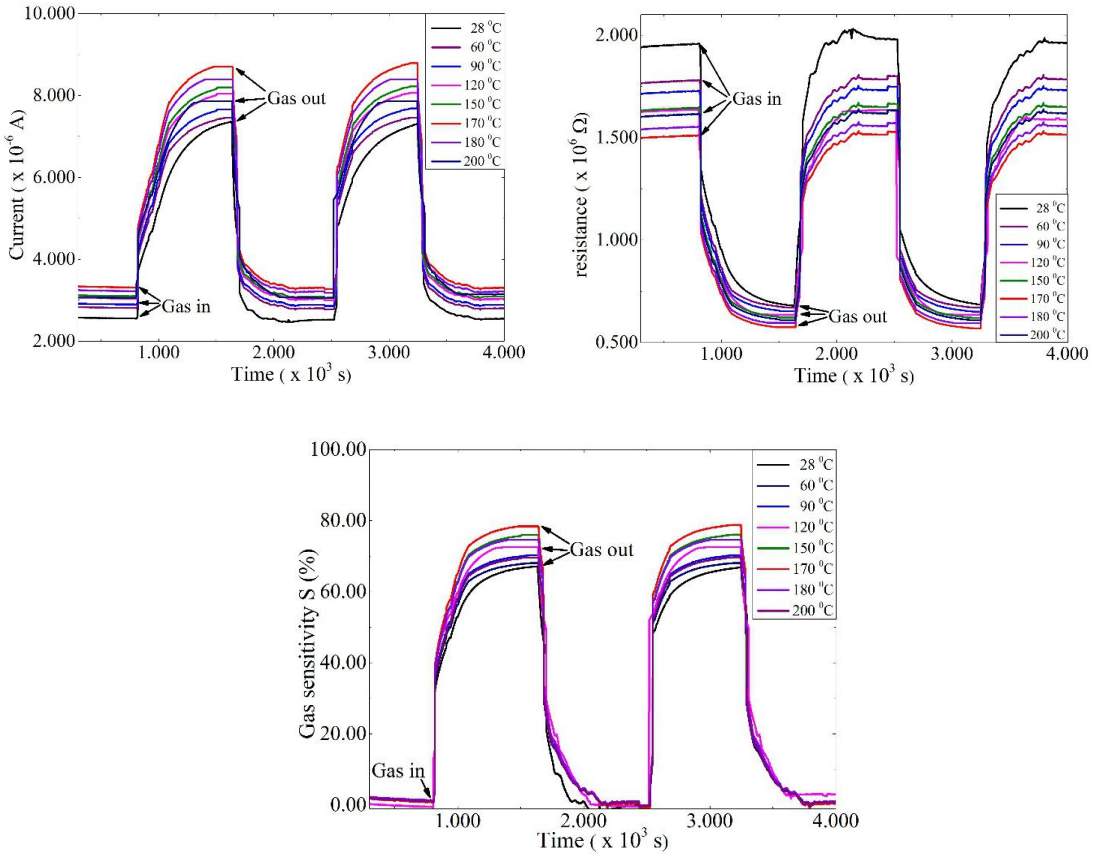

Figure 4: Variation of the current, resistance and gas sensitivity with time for CO_2 gas at different operating temperatures.

This can also be explained using the chemisorption and physisorption. The gas sensing mechanism depends on the surface reaction between chemisorbed oxygen and reducing gases. The adsorption of oxygen on the film surface has two forms: physisorption and chemisorption. At elevated temperature, chemisorption is dominant. The transition from physisorption to chemisorption needs activation energy, which can be accomplished by increasing the operating temperature. It has been observed that the amount of oxygen adsorbed on the sensor surface goes on increasing with an increase in temperature, and reaches to maximum. However, when the temperature is very high, the

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oxygen atoms leave the surface of the gas sensor, and gas sensitivity decreases with further increase in the operating temperature.

Figure 5 represents the curve of gas sensitivity versus operating temperature for CO_2 gas. Table 2 shows the gas sensitivity, response time and recovery time of $\alpha-Fe_2O_3$ gas sensor in CO_2 gas. The maximum gas sensitivity in CO_2 gas obtained at 170 ^{0}C temperature is 78.22%. At this temperature, the gas sensitivity increased by a factor of 1.17 compared with the gas sensitivity at the room temperature. The response and recovery times decrease when increasing the operational temperature. At room temperature, response and recovery times are 819, 619 s respectively. At 170 ^{0}C temperature, response and recovery times reach the minimum values. Gas sensors with highest sensitivity and lowest respond and recovery time are the best gas sensors. Therefore, all the properties of the $\alpha-Fe_2O_3$ gas sensor can be optimized at 170 ^{0}C. The maximum sensitivity obtained for CO_2 gas by us is really larger than those obtained by some other researches [33, 34, 35]. But the response and recovery times reported in those reports for CO_2 gas are slightly better than those of our samples measured in CO_2 gas.

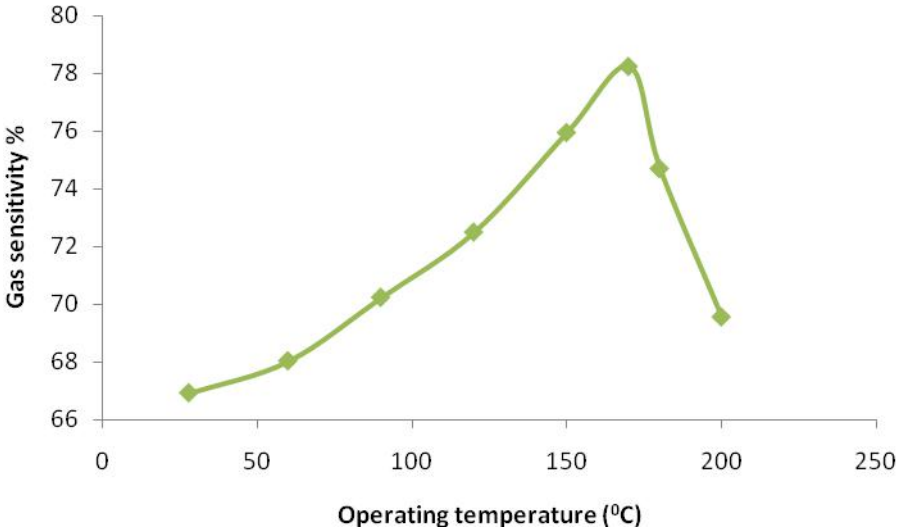

Figure 5: Curve of gas sensitivity versus operating temperature for CO_2 gas.

Table 2: Gas sensitivity, response time and recovery time of $\alpha-Fe_2O_3$ gas sensor in CO_2 gas.

Operating temperature (^{0}C)	Response time (s)	Recovery time (s)	Gas sensitivity (%)
28	819	619	66.91
60	803	606	68.02
90	792	597	70.22
120	758	563	72.48
150	723	538	75.93
170	686	511	78.22
180	743	548	74.68
200	811	605	69.54

4. Conclusion:

Gas sensitivity, response time and recovery time of $\alpha-Fe_2O_3$ thin films were measured in 1000ppm of different gas species such as CO_2, acetone, ethanol and methanol vapors at the room temperature. $\alpha-Fe_2O_3$ is highly sensitive to CO_2 gas compared to acetone, ethanol and methanol vapors. The gas sensitivity of $\alpha-Fe_2O_3$ thin films is 66.91% in CO_2 gas. $\alpha-Fe_2O_3$ indicates the lowest sensitivity of

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32.04% in the methanol vapor at the room temperature. The best response time (69 s) and recovery time (86 s) can be observed in the ethanol vapor at the room temperature. The gas sensitivity, response time and recovery time of $\alpha-Fe_2O_3$ thin films were measured in 1000ppm of CO_2 at different operating temperatures. The lowest sensitivity of 66.91% was observed at the room temperature, and the highest sensitivity of 78.22% was observed at 170 ^{0}C. The gas sensitivity gradually increased from the room temperature to 170 ^{0}C and then decreased with the further increase of the operating temperature. The best response time (686 s) and recovery time (511 s) were also obtained at 170 ^{0}C. The transition from physisorption to chemisorption needs activation energy, which can be accomplished by increasing the operating temperature. As a result, the gas sensitivity increases with the operating temperature. When the temperature is further increased O_2 atoms move out from the surface of the material. As a result, the gas sensitivity decreases when the temperature is further increased.

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