CHAPTER 5

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Recent research opens a new window to replace the conventional devices by nano devices (quantum dots) due to their manifold advantages such as, faster switching speed, higher efficiency, lower power consumption, smaller size etc.[1-42]. In this chapter an attempt has been made to study and discuss the gas sensing phenomenon of our prepared quantum dots. It has been observed that these gas sensors are of distinct advantages over the conversional ones[5,6]. Although a number of other gas sensors (such as thin film) have been studied, but quantum dot gas sensor are yet to be investigated extensively. Hence, the present work is of recent interest.

A Gas sensor is a component that converts the presence of a gas or vapor into an electrically measurable signal. It is well known [1,2] that the resistance of semiconductor is very sensitive to chemical reaction (adsorption and desorption) of the gaseous ambient surrounding it and so when semiconductor materials are used as gas sensors, these are found to detect a wide variety of gases / vapors [3-42]. In this chapter the sensing properties of our prepared semiconductor quantum dots to three types of reducing gas / vapors [13] are studied which is my contribution to this chapter. The study is restricted in case of reducing gases only due to limitation of time during the research work. Among all, the following three reducing gases are considered in the present study:

(i) Acetone (CH_3COCH_3)

(ii) Ethanol (C_2H_5OH), and

(iii) Methanol (CH_3OH)

The above three gases have been chosen because

1. These are hazardous to health and so sensing of these gases is very important
2. For diagnosis of some common disease (e. g diabetes) the above mentioned gases are needed to be sensed frequently.

5.1 Basic principle of solid state semiconductor gas sensor

The basic principle of semiconductor gas sensor is the change in resistance of the sensor material that arises from the change in electron concentration near the sensor surface by the adsorption and desorption (reaction) with gases or vapors. When n-type semiconductor materials (our samples) are used as gas sensors, basically two kinds of sensing mechanism are found to be taken place [3-5].

a. Adsorption: In the absence of test gas, the atmospheric oxygen gets adsorbed (chemisorbed) on the sensor surface and acquire electron from the conduction band of the n-type semiconductor gas sensors, thereby forms ionic species such as O^{2-}, O_2^-, and O^- etc. This phenomenon reduces the concentration of the number of charge carriers near the surface (conduction band) giving rise to increase in the overall resistance of the sensor. Adsorption is temperature dependent. It is also material dependent and hence it is not same for all the sensors materials i.e ZnO, SnO_2 or Fe_2O_3. Adsorption takes place by the following equations:

$$O_2\,(gas) \leftrightarrow O_2\,(ads) \quad \text{.....(5.1)}$$

$$O_2\,(ads) + e^- \leftrightarrow O_2^-\,(ads) \quad \text{.....(5.2)}$$

$$O_2^-\,(ads) + e^- \leftrightarrow 2O^-\,(ads) \quad \text{.....(5.3)}$$

The formation of O^{2-} species is also possible as follows

$$O^{-}(ads) + e^{-} \leftrightarrow O^{2-} \text{.....(5.4)}$$

e^{-} is the acquired electron by oxygen from conduction band of sensor (quantum dots) resulting in higher sensor resistance .

(b). **Desorption:** On injection of the reducing gas (vapor), such as acetone, ethanol, methanol, etc in the gas sensing chamber (tubular furnace), reacts with the chemisorbed oxygen on the sensor surface and injects the carrier to the sensor. This phenomenon is called "desorption" which results in the decrease in sensor (e. g quantum dot) resistance which is a measure of gas sensitivity or sensor response. During desorption, reducing gas acting on the oxide's sensor surface under goes the following reaction.

$$R + O^{-}(ads) \leftrightarrow RO + e^{-} \text{ .....(5.5)}$$

Where R is the reducing gas, e^{-} are electrons injected to the sensor surface (conduction band).

Both adsorption and desorption are material dependent property.

5.1.1. Ad**vantage of quantum dot gas sensor**: Adsorption and desorption are absolutely surface phenomena [11,13,17,38]. In quantum dot (quantum dot film) due to large surface area (S/V ratio) [19,26] adsorption and desorption occur very fast and effectively resulting in sharp and fast change in the resistance and thereby producing fast response (sensitivity) with small changes in pre-heating temperature or concentration of vapor (e.g ethanol). Large S/V ratio is the key reason for which

quantum dots are of recent interest for gas sensing with high efficiency and fast response speed. Smaller the size of quantum dot larger is the S/V ratio.

5.2. Instrumentation for gas sensing

The experimental setup generally employed to study the gas sensing properties are by the two systems

(i) **Dynamic flow system:** In a dynamic flow system, the test gas or vapor is mixed with dry air and passed in to the chamber with a constant flow rate.

(ii) **Static system:** In a static system, the test gas is mixed with dry air and is introduced into the chamber.

In the present work, the gas sensing measurement is carried out using a static system. The schematic diagram of the static measurement setup used to measure the response of the test gas/ vapors is shown in figure 5.1.

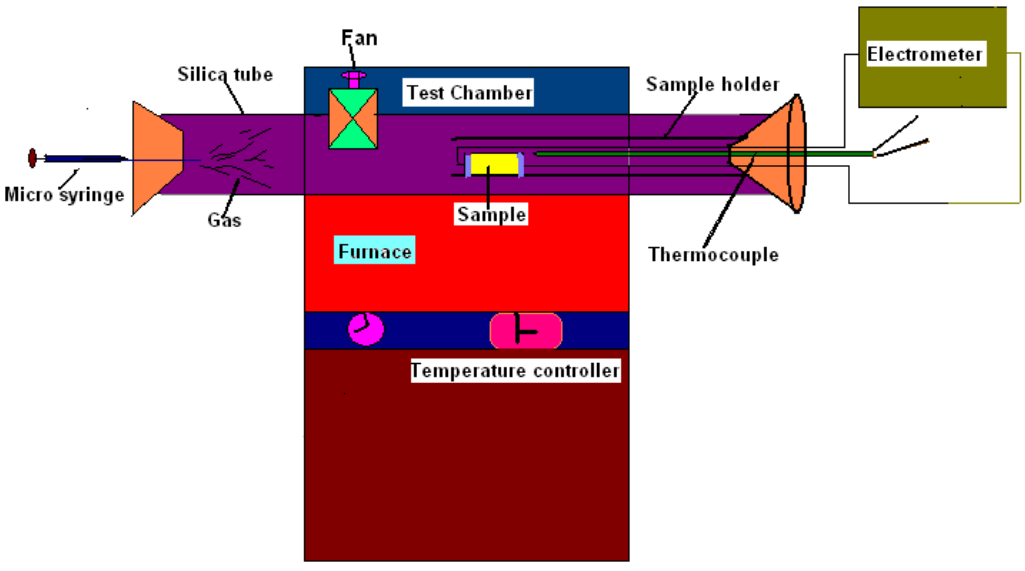

Fig.5.1. Schematic representation of static measurement setup.

To prepare the quantum dot sensor (sample) for gas sensing, the film of quantum dots on the glass substrate is cut in the size of 1 cm x 1cm and it (sample / sensor) is mounted on a two-probe sample holder placed into a silica tube which is inserted coaxially inside a tubular furnace. The furnace temperature is controlled within $\pm 1^0$C and the temperature variation over the length of the films is found to be within $\sim \pm 1^0$C. For sensing, a known volume of the test gas or vapor is allowed to enter into the closed silica tube and subsequently the decrease in film resistance is monitored till it becomes stable. Lastly, both ends of the tube are opened and the film resistance is allowed to recover the initial value in air. The electrical resistance of the films is measured before and after exposure to gas/vapor using a Keithley System Electrometer (Model: 6514). The sensor response of the film is determined at different operating temperatures in the range 180–400^0C to various concentrations of gas / vapor in air [8,9].

5.3. Sensing parameters:

(a) Sensitivity/Response

The sensitivity (S) of a sensor is defined as the ratio of the change in the resistance(ΔR) of the sensor in the presence of the gas or vapor to the original resistance(R) at that temperature and for a specific concentration.

$$\text{i.e} \quad S = \Delta R / R \quad \ldots\ldots\ldots (5.6)$$

In the present study, the sensitivity of quantum dots (quantum dot film) is determined using following equation as all the test gas/vapors possess the properties of reducing gas [8].

$$S = \frac{(R_a - R_g)}{R_a} \times 100\ \% \qquad \text{……..(5.7)}$$

Where, R_a = resistance of quantum dot film in air, R_g = resistance of quantum dot film upon exposure to gas / vapor. Every time prior to exposing the quantum dots (quantum dot film) to the test gas/ vapor, it has been allowed to equilibrate inside the gas chamber at operating temperature for 30 minute and the stabilized resistance is taken as R_a [10]. The sensitivity generally varies with two parameters [3-9].

(i) Operating temperature and

(ii) Concentration of the gas or vapor.

(b) Response time (T_{res})

The response time to a test gas/vapor is defined as the time taken to reach 90% of saturation resistance (R_g) on exposure to gas/ vapor. It is measured by the time required to reach 90% of the response before reaching the saturation.

(c) Recovery time (T_{rec})

The recovery time to a test gas / vapor is defined as the time taken to reach the 10% of the initial resistance (R_a) on removal of the gas/ vapor. It is measured by the time required to reach 10% of the response from saturation on removal of the gas /vapor.

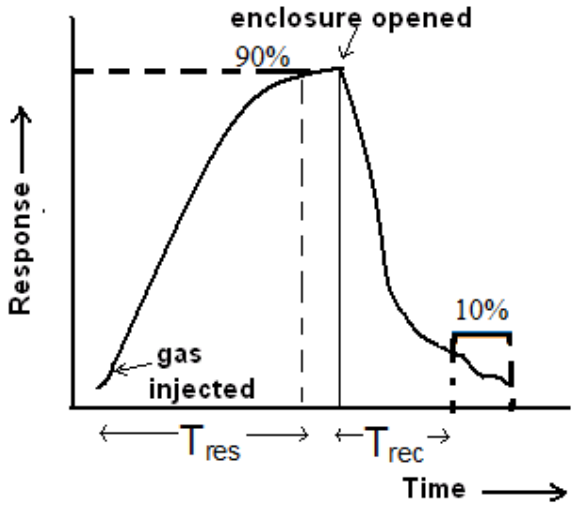

Fig.5.2. A typical transient response characteristic curve.

The response time as well as recovery time are found to be dependent upon [9,10] .

(i) Sensor operating temperature and

(ii) Concentration of the test gas/vapor.

The response and the recovery times are important parameters for designing sensors for the desired applications. For efficient gas sensor, the sensitivity should be high while response and recovery time should be small.

Response and recovery time greatly depend on the electron mobility in the gas sensing material. Higher the mobility smaller is the response and recovery time. In the present study, there are two types of electron mobility:

i. Electron mobility through quantum dots (sensor)

ii. Electron mobility through the matrix embedding quantum dots. Though neither PVA (Polyvinyl Alcohol) nor PVP (Polyvinyl Pyrrolidone) is conductor (i.e electron can not move) but in the present case due to very thin thickness (less than 10 nm as seen in HRTEM image in figure 5.3) of matrix, electron can tunnel from one

quantum dot to another. Thinner the matrix, less is the response (also recovery time) time. Thus, along with sensor material the matrix thickness also controls the response and recovery time in the present study. At high temperature (250^0C and above), PVA matrix (embedding ZnO quantum dots) tends to destroy (burns due to heating at high temperature e.g 200 ^{0} C) but the electrical property (i.e. acetone sensing) of ZnO quantum dot film (sample) is not affected [18,42] because charge carriers (electrons) can still tunnel from one dot to another dot through the burnt matrix layer.

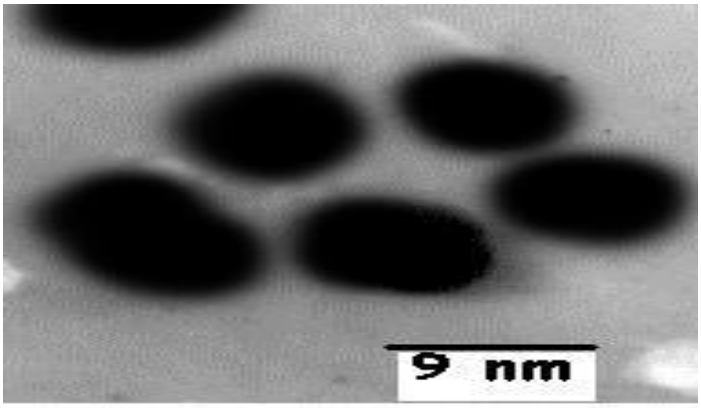

Fig 5.3 : HRTEM image of ZnO/PVP quantum dots

In our present study, apart from the above mentioned parameters (i.e operating temperature and gas / vapor concentration etc.) the following material (sensing material) parameters also control the gas sensing mechanism. These are:

1. Size of quantum dots
2. Band gap of material
3. Material work function
4. Ionic radius of material
5. Permeability of material

The above mentioned parameters depend on fabrication techniques.

Furthermore, sensing mechanism depends on nature of gas (viz. acetone, ethanol, methanol etc.)

5.4 Measurement of gas / vapor Volume

The amount of test gas /vapor (acetone, ethanol and, methanol) to be injected into the gas chamber is measured by a micro-syringe. The concentration of the above mentioned vapors is measured in parts per million (ppm).

To study the gas sensing property of a gas sensor, basically two kinds of characteristics are suited (after injection of gas). These are:

1) **Variation of sensitivity with operating temperature**
2) **Transient response characteristic.**

1. Variation of sensitivity with operating temperature

In this characteristic sensitivity is observed as a function of operating temperature for a specific concentration (ppm) of test gas as shown in figure 5.4

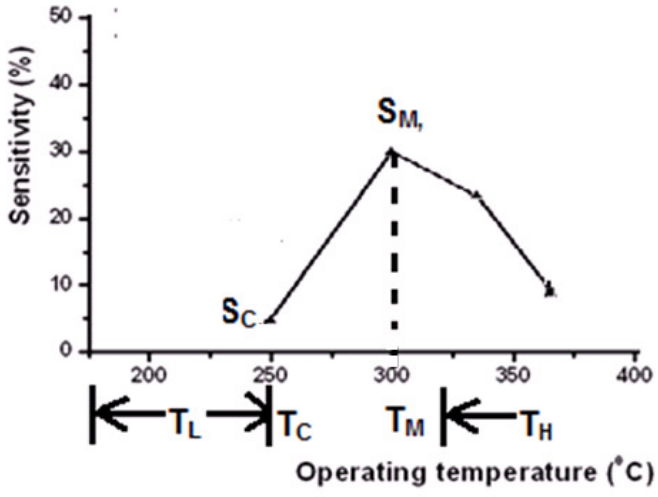

Fig.5.4 Schematic of Variation of sensitivity with operating temperature

At relatively low operating temperature ($\mathbf{T_L}$), the sensitivity of the quantum dot sensor is restricted by the nature of adsorption and desorption (in absence and presence of test gas respectively). When the sample (sensor) is heated up to certain temperature **($\mathbf{T_C}$)**, adsorption and desorption occur very fast and effectively resulting in practical sensitivity [8] (S_C). The sensitivity is as already been defined by the equation.

$$S = \frac{(R_a - R_g)}{R_a} \times 100\ \%$$

Where, R_a = resistance of quantum dot film in air,

R_g = resistance of quantum dot film upon exposure to gas / vapor

It is observed that at a certain specific temperature (T_M), sensitivity of the sensor (quantum dots) is maximum(S_M). This is attributed to the availability of sufficient adsorbed ionic species of oxygen on sensor (e.g ZnO quantum dot film) surface which reacts (desorbs) most effectively and rapidly with test gas / vapor molecules at this specific temperature. At a higher temperature above T_M , the adsorbed oxygen species available at the sensing sites on the quantum dot surface, are not enough to react (desorbs) with test gas / vapor molecules [12].This results into a small change in resistance and hence less is the sensitivity. The schematic of the characteristic is shown in figure 5.4.

(b) Transient response characteristic.

The transient response characteristic is the plot between sensitivity and time. This characteristic indicates the response and recovery time. The response time is measured as the time required reaching 90% of the total response before reaching

the saturation. In the figure 5.5 90% reaches at point A while saturation reaches at B. Response time is $T_{res.}$ Recovery time indicates the time required to reach 10% of the saturation value on removal of the gas / vapor. In fig, C indicates 10% of the total response (saturation). T_{rec} indicates the recovery time.

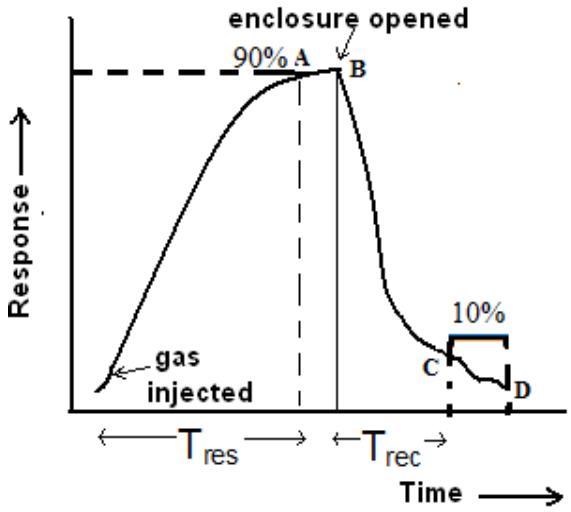

Fig.5.5. Schematic of transient response characteristic

5.5. ZnO Quantum dots for gas sensing:

5.5.1 Acetone sensing properties of ZnO Quantum dots embedded in PVA matrix

To test acetone sensing, ZnO sample is mounted on a two-probe sample holder placed into a silica tube which is inserted coaxially inside a tubular furnace as explained in section 5.2. The furnace temperature is controlled within $\pm 1^0$C and the temperature variation over the length of the sample is found to be within $\pm 1^0$C. A known volume (parts per million, in short "ppm") of acetone is put with the help of a micro-syringe into the closed silica tube. The electrical resistance of the sample is

measured before and after exposure to acetone using a Keithley System Electrometer (Model: 6514). The sensing response of ZnO quantum dots (film of quantum dots) is determined at different operating temperatures in the range 200–360^{0}C to various concentrations of acetone in air [8,1].

To study sensing [5-36] of acetone (test gas), at first, ZnO quantum dot film (sample) is heated in the chamber of tubular furnace in air in the absence of acetone and atmospheric oxygen is adsorbed chemically [17] on ZnO (as it is of n type specimen) surface. The adsorbed oxygen forms ionic species such as O2−, O2−and O− by the following reaction kinematics [17,41].

$O_2(gas) \leftrightarrow O_2(ads)$ ……(5.8)

$O_2(ads) + e- \leftrightarrow O_2-$ ……...(5.9)

$O_2^-(ads) + e- \leftrightarrow 2O-(ads)$ ……..(5.10)

These oxygen species desorbs upon exposure to acetone vapor (gas) and results in decrease of ZnO quantum dot resistance [11,17,41] because acetone is reducing in nature. The desorption process occurs in one of the following ways depending on operating temperature [17]

$CH_3COCH_3(gas) + O- \rightarrow CH_3\,COCH_2 + OH- + e-$ …….. (5.11)

$k = 1.0\times10^{12}\, e^{(-21,000/RT)}$ [cm^3/mol s]

$CH_3COCH_3(gas) + OH^- \rightarrow CH_3CHO + CH_3O-$ ……. (5.12)

$k = 2.0\times10^{12}\, e^{(-63,000/RT)}$ [cm^3/mol s]

$CH_3CHO + O(bulk) \rightarrow CH_3COOH + O(vacancies)$ …… (5.13)

$CH_3COCH_3\,(gas) + O- \rightarrow CH_3{}^+CO + CH_3O- + e-$ ……(5.14)

$k = 1.0 \times 10^{12}\, e^{(-42,000/RT)}$ [cm^3/mol s]

$CH_3^+CO \rightarrow CH_3^+ + CO \quad k = 2.0 \times 10^{11} e^{(-15,000/RT)}$ [1/s] …….(5.15)

$CO + O \rightarrow CO_2 + e-$ ……(5.16)

It is clear that in all the cases Eqs. (5.11), (5.14) and (5.16) acetone reacts with chemisorbed oxygen in ZnO quantum dot surface, inject charge carrier (e−) to ZnO specimen and thereby reducing the sensor resistance. Thus, the "response" [10,13] is (as defined already)

$$[((Ra - Rg)/Ra) \times 100]\%.$$

Where Ra is the ZnO quantum dot resistance in air and Rg is the resistance upon exposure to acetone. When the acetone is released by opening the enclosure of the sensing chamber, the reverse process takes place and the sensor (ZnO) resistance regains its original value.

(a) Variation of sensitivity with operating temperature

The sensing characteristics of ZnO film as a function of operating temperature for three different concentrations, namely 100, 300, and 500 ppm of acetone in air is represented in figure 5.6.

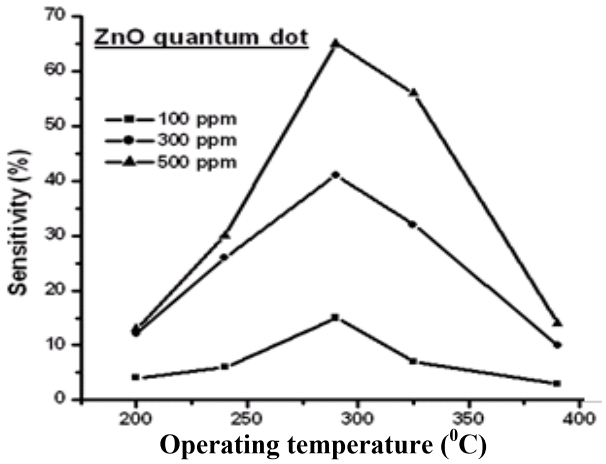

Fig.5.6 Variation of sensitivity with operating temperature at different acetone concentration

At relatively low operating temperature of 200^0C, the sensitivity of the quantum dot sensor is restricted by the nature of the chemical reaction (adsorption and desorption process). When the sensor (quantum dot film) is heated above 200^0C, the chemical reaction occurs very fast and effectively resulting in an increase in the sensitivity [8]. At temperature of 290^0C, sensitivity of the sample is maximum. This is attributed to high desorption i.e effective and rapid chemical reaction between acetone molecule and adsorbed oxygen species available on ZnO quantum dot film surface generating large numbers of charge carriers (e−) resulting in rapid change (decrease) in sample (quantum dot film) resistance and hence higher is the response (efficiency). At higher temperature above 290^0C, the adsorbed oxygen species available at the sensing sites on the quantum dot surface, are not enough to react with acetone vapor molecules [12]. This results decrease in sensitivity.

It is observed that at lower concentration of acetone vapor, the sensitivity is less, while at higher concentration [12] the sensitivity is high. This phenomenon occurs due to the fact that at lower concentration (100 ppm), the surface reaction proceeds slowly but at higher concentration,(300 ppm, 500 ppm), because of increase of surface coverage of molecules [12,41] surface reaction proceeds faster and very effectively resulting in higher sensitivity. For a particular concentration of acetone, say 100 ppm, the sensitivity first increases from 5% to 13 % as the temperature is raised from 200 to 290^0 C and then decreases to 3 % when the temperature is further raised to 370^0 C. In this case the optimum operating temperature is 290^0 C at which the sensitivity is found to be maximum for each concentration of acetone [42]. The quantum dots shows a maximum sensitivity of 65% for 500 ppm of acetone at 290^0 C.

(b) Transient response characteristics.

Figure 5.7 represents the transient response characteristics of ZnO quantum dot to acetone concentration of 100, 300 and 500 ppm at 290^{0}C. Examining the graphs, it is revealed that the response time and recovery time decrease with higher concentration. This is attributed [12,38] to the fact that higher concentration favors and accelerates desorption. Transient response characteristic indicates that response time and recovery time of ZnO quantum dot acetone sensor is very less (as evident from figure 5.7 an it is less than 1 minute which is much smaller than the response time of ZnO thin film acetone sensor [17,41].

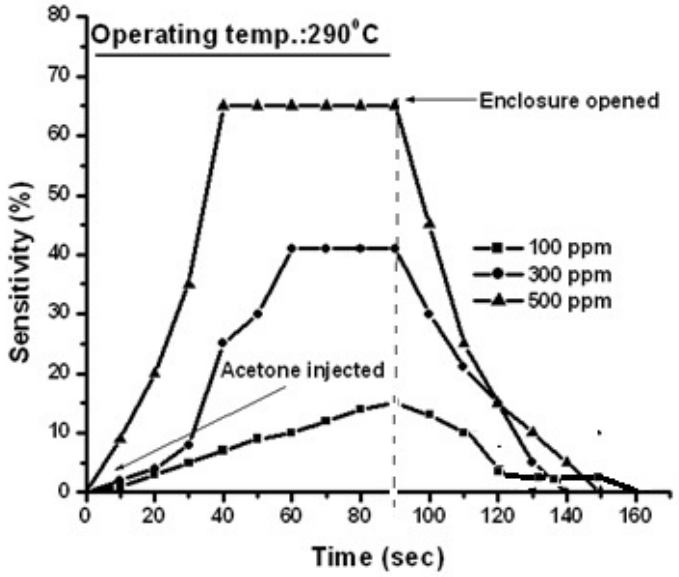

Fig. 5.7. Transient response characteristics ZnO/PVA quantum dot to different acetone concentrations of acetone in air at 290 ^{0}C.

Table (5.1) summarizes the data of sensitivity Vs operating temperature plot and transient response at different acetone concentration.

Acetone concentration (ppm)	Temperature of Maximum sensitivity (T_M)	Maximum sensitivity (%) (S_M)	Response time (Sec)	Recovery time (Sec)
100 ppm	290^0C	13	85	60
300 ppm	290^0C	42	55	50
500 ppm	290^0C	65	35	40

Table 5.1: data of sensitivity Vs operating temperature plot and transient response at different acetone concentration for ZnO/PVA sensor

5.5.2 Acetone sensing properties of ZnO Quantum dots Embedded in PVP matrix.

Though the sensing mechanism and process of ZnO on PVP are the same as ZnO on PVA but the sensing parameters (i.e characteristics) differ significantly. The next section explains the acetone sensing phenomenon of ZnO on PVP. Sample is mounted on a two-probe sample holder placed into a silica tube which is inserted coaxially inside a tubular furnace as explained earlier.

(a) **Variation of sensitivity with operating temperature**

Figure 5.8 represents the response characteristics as a function of operating temperatures for three different concentrations of 100, 300 and 500 ppm of acetone vapor as explained in case of ZnO/ PVA. At relatively low operating temperature around 230^0C, the response of ZnO quantum dot is restricted by slow chemical reaction (adsorption and desorption) while above 230^0C, the chemical reaction occurs very fast and efficiently resulting in higher response[8,40]. At 300^0C the response is maximum. This is attributed to the availability of sufficient adsorbed ionic species of oxygen on ZnO surface which reacts most effectively and rapidly

with acetone molecules at this particular temperature [17,40] . At higher temperature above 300^0C, the adsorbed oxygen species available at the sensing sites on the quantum dot surface, are not enough to react with acetone vapor molecules [12].This results into a small change in resistance and hence less is the sensitivity.

Further, it is observed that at lower concentration of acetone vapor, the sensitivity is less while at higher concentration[12] the sensitivity is high. The reasons are explained in case of PVA embedded ZnO sensor.

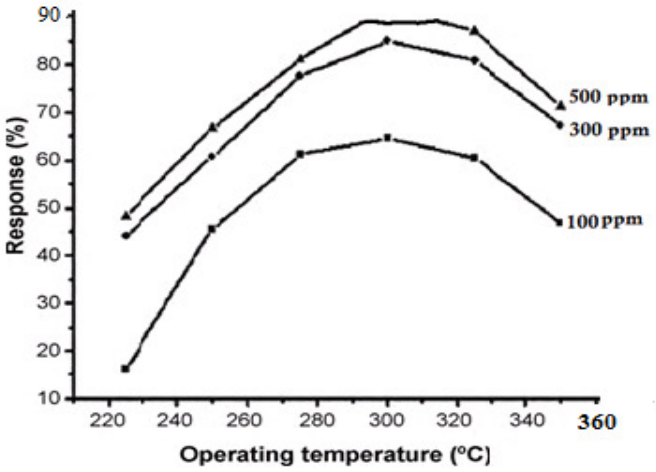

Fig: 5.8-Response versus operating temperature at various concentrations of acetone vapor

(b) Transient response characteristics:

Figure 5.9 represents the transient response characteristics of ZnO quantum dot to acetone concentration of 100, 300 and 500 ppm at 300^0C. Examining the graphs, it is revealed that the response time and recovery time decrease with higher concentration. This is attributed[12,40] to the fact that higher concentration favors and accelerates the desorption of the reaction products producing less response and recovery time.

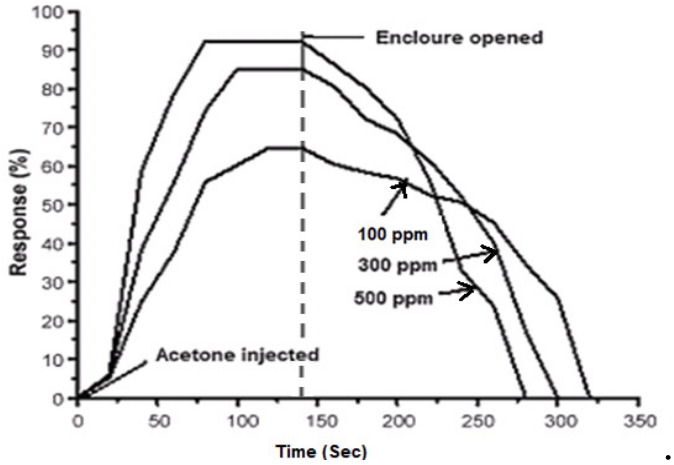

Fig 5.9- Transient response characteristics of the ZnO/PVP quantum dot for various acetone concentrations at 300^0C.

Response characteristic indicates that response time of ZnO quantum dots acetone sensor is very less (as evident from Figure 5.9) which is much smaller than that of ZnO thin film acetone sensor [17].

Table (5.2) summarizes the data of sensitivity Vs operating temperature plot and transient response at different acetone concentration..

Acetone concentration (ppm)	Temperature of Maximum sensitivity (T_M)	Maximum sensitivity (%) (S_M)	Response time (Sec)	Recovery time (Sec)
100	300^0C	62	110	175
300	300^0C	82	85	140
500	300^0C	88	60	120

Table 5.2 The data of sensitivity Vs operating temperature plot and transient response at different acetone concentration for ZnO/PVP sensor

5.5.3 Advantage of ZnO/PVP quantum dot sensor over ZnO/PVA quantum dot sensor

From the above studies, some advantages and disadvantages of ZnO/PVP quantum dots sensor over ZnO/ PVA quantum dots sensor have been observed. These are:

1. ZnO/ PVP sensor has better acetone sensitivity in compare to the sensitivity of ZnO/ PVA sensor. This is due to formation of quantum dots of smaller size in a well uniformed array in PVP matrix
2. Further, ZnO/PVP quantum dot sensor are stable for two years or so while ZnO/ PVA quantum dot sensor is stable for six months or so.

Considering the advantages, PVP matrix has been used in subsequent works. However, if extremely small response and recovery time required, PVA matrix may be chosen. A comparative table for ZnO in PVA as acetone sensor and ZnO in PVP as acetone sensor is given below.

	ZnO Q.D Embedded on PVA			ZnO Q.D Embedded on PVP		
	Acetone Concentration			Acetone concentration		
	100 Ppm	300 ppm	500 ppm	100 ppm	300 ppm	500 ppm
Response in %	13	42	65	62	82	88
Operating temperature (^{0}c)	290	290	290	300	300	300
Response time (sec)	85	55	35	110	85	60
Recovery time (sec)	60	50	40	175	140	120

Table 5.3: Comparative table for ZnO/PVA as acetone sensor and ZnO/PVP as acetone sensor

5.5.4. Ethanol sensing properties of ZnO Quantum dots Embedded in PVP matrix.

To test ethanol sensing, ZnO sample is mounted on a two-probe assembly placed in sample holder into a silica tube which is inserted coaxially inside a tubular furnace and ethanol is injected in to tubular furnace in the similar process as explained earlier. The sensing response of ZnO quanum dots is determined at different operating temperatures in the range 220–360^{0}C to various concentrations of ethanol [21,23,28,37]. To study sensing [8-21,37], at first, ZnO quantum dot sample is heated in a chamber in air in the absence of test vapor when atmospheric oxygen is adsorbed chemically [21,37] on ZnO surface. The adsorbed oxygen forms ionic species such as O^{2-}, O_2^- and O^- by the reaction kinematics explained already [5,37] by equation (5.8),(5.9),(5.10). These oxygen species desorbs upon exposure to ethanol and results in decrease of ZnO quantum dot resistance [5,11,28,37] as ethanol is reducing in nature. The desorption process occurs in the following way [21,37] .

$$C_2H_5OH\ (gas) + O^- \leftrightarrow CH_3CHO + H_2O + e^- \quad \ldots\ldots\ldots\ldots\ldots (5.17)$$

From equation (5.17) it is clear that ethanol reacts with chemisorbed oxygen in ZnO quantum dot surface, inject charge carrier (e^-) to ZnO specimen and thereby reducing the sensor resistance. When the ethanol is released by opening the enclosure of the tubular furnace, the reverse process takes place and ZnO quantum dot resistance regains its original value and thus, the ZnO/ PVP acts as ethanol sensor with sensitivity define by equation

$$S = \frac{(R_a - R_g)}{R_a} \times 100\ \%$$

Where R_a = resistance of ZnO/ PVP quantum dot film in air,

R_g = resistance of quantum dot film upon exposure to acetone

(a) Variation of sensitivity with operating temperature

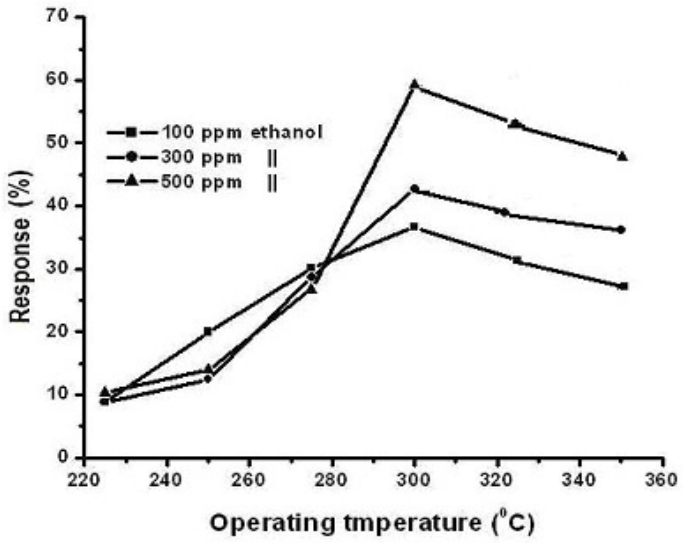

Fig 5.10. Response Vs operating temperature for different ethanol concentrations

Figure 5.10 represents the response characteristics as a function of operating temperatures for three different concentrations of 100, 300 and 500 ppm of ethanol vapor. At relatively low operating temperature around 230^0C, the response of ZnO quantum dot is restricted by slow desorption while above 230^0C, the desorption occurs very fast and efficiently resulting in higher response[11,37]. At 300^0C the response is maximum. As explained earlier, this is attributed to the availability of sufficient adsorbed ionic species of oxygen on ZnO surface which reacts (desorbs) most effectively and rapidly with ethanol molecules at this particular temperature [21] and produces large numbers of charge carriers (e^-) resulting in rapid change (decrease) in sample resistance and hence higher is the response.

At temperature higher than 300^0C, the amount of adsorbed (chemisorbed) oxygen is decreased with increasing temperature and change in surface coverage in chemisorbed oxygen becomes smaller, leading to smaller response. Further, it is

observed that at lower concentration of ethanol vapor, the sensitivity is less, while at higher concentration [12] the sensitivity is higher. This phenomenon occurs due to the fact that at lower ethanol concentration (100 ppm), the surface reaction proceeds slowly but at higher concentration, (300 ppm), because of increase of surface coverage of molecules[12,42] surface reaction proceeds faster and very effectively resulting in higher sensitivity.

(b)Transient response characteristics:

Figure 5.11 represents the transient response characteristics of ZnO quantum dot to ethanol concentration of 100, 300 and 500 ppm at 300^0C. Examining the graphs, it is revealed that the response time decrease with higher concentration. This is attributed [10,37] to the fact that higher ethanol concentration favors and accelerates the desorption process resulting in faster response i.e less response and recovery time.

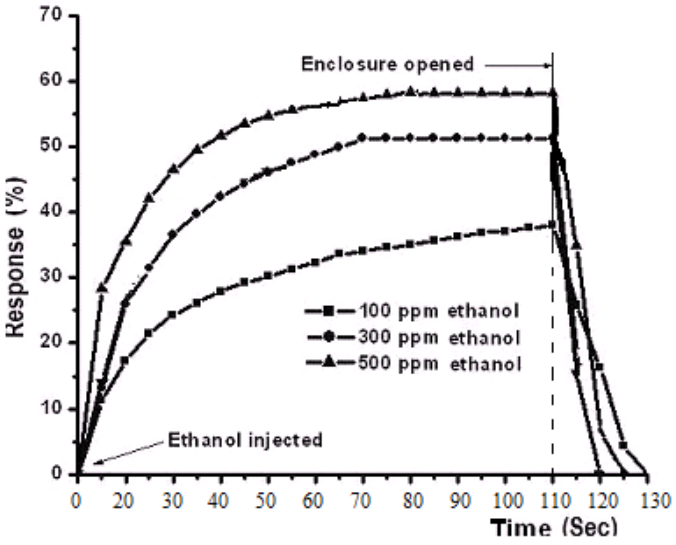

Fig 5.11 Transient response characteristics of ZnO quantum dots for different concentrations of ethanol at 300^0C

Table (5.4) summarizes the data of sensitivity Vs operating temperature plot and transient response at different ethanol concentration..

Ethanol concentration (ppm)	Temperature of Maximum sensitivity (T_M)	Maximum sensitivity (%) (S_M)	Response time (Sec)	Recovery time (Sec)
100	300^0C	37	80	17
300	300^0C	45	50	12
500	300^0C	60	40	7

Table 5.4 : Data of sensitivity Vs operating temperature plot and transient response at different ethanol concentration for ZnO/PVP sensor

5.5.5 Methanol sensing properties of ZnO Quantum dots Embedded in PVP matrix.

To test methanol gas sensing [12,8] ZnO quantum dots sample is mounted on a two-probe assembly placed in sample holder into a silica tube and methanol is injected in to the tubular furnace in the similar way as explained already. Sensing response of ZnO quantum dots is determined at different operating temperatures in the range 200–360^0C to various concentrations of methanol. At first, ZnO quantum dots sample is heated in the chamber in air in absence of methanol vapor, and atmospheric oxygen is adsorbed chemically on ZnO surface. The adsorbed oxygen form ionic species such as O2-, O2- and O- by the reaction kinematics as explained earlier by equation no [11,15] (5.8),(5.9) and (5.10). Next, these oxygen species desorbs upon exposure to methanol vapor (gas) that results in decrease of ZnO quantum dot resistance[7,8,11,24,27] as methanol is reducing in nature. The desorption process occurs in one of the following two ways depending on operating temperature [8] .

CH3OH + O−(adsorbed) _ HCOH + H2O + e−…….[5.18]

CH3OH+ O2−(adsorbed)_ HCOOH + H2O + e−……..[5.19]

It is evident from equation (5.18) and (5.19) that methanol is oxidized to formic acid, liberating electrons on ZnO surface, thereby decreasing its resistance. When the gas is released by opening the enclosure of the sensing chamber, the reverse process takes place and specimen (quantum dot) resistance regains its original value.

$$S = \frac{(R_a - R_g)}{R_a} \times 100\ \%$$

Where, R_a = resistance of ZnO/ PVP quantum dot film in air,

R_g = resistance of quantum dot film upon exposure to methanol

(a) Variation of sensitivity with operating temperature

Figure 5.12 represents the response characteristics as a function of operating temperature for three different concentrations of 100, 300 and 500 ppm of methanol vapor.

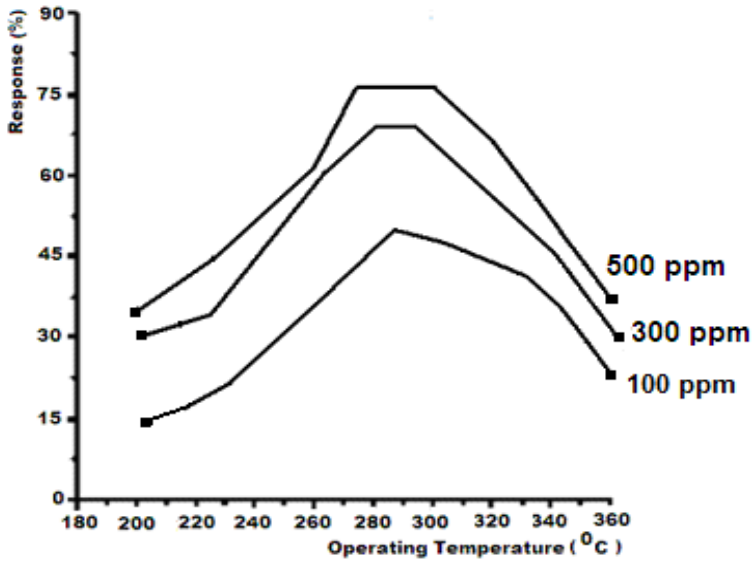

Fig 5.12 Response Vs operating temperature for different methanol concentrations

At relatively low operating temperature around 200^0C, the response of ZnO quantum dot is restricted by slow chemical reaction (desorption) while above 200^0C, the reaction occurs very fast and efficiently resulting in higher *response* [22]. At around 290^0C the response is maximum. This is attributed to the availability of sufficient adsorbed ionic species of oxygen on ZnO surface which reacts most effectively and rapidly with methanol molecules at this temperature [13,22] and produces large numbers of charge carriers (e-) resulting in rapid change (decrease) in sample resistance and hence higher response. At temperature higher than 300^0C, the amount of adsorbed (chemisorbed) oxygen is decreased with increasing temperature, surface coverage in chemisorbed oxygen becomes smaller leading to smaller response. It is observed that at lower concentration of methanol vapor, the sensitivity is less, while at higher concentration [12] the sensitivity is higher. This phenomenon occurs due to the fact that at lower concentration (100 ppm), the surface reaction proceeds slowly but at higher concentration,(300 ppm higher), because of increase of surface coverage of molecules [12,42] surface reaction proceeds faster and very effectively resulting in higher sensitivity.

(b) Transient response characteristics

Figure 5.13 represents the transient response characteristics of ZnO quantum dots to methanol concentrations of 100, 300 and 500 ppm at 290^0C. The graphs infer that response time and recovery time decrease with higher concentration. This is attributed[15,31] to the fact that higher concentration favors and accelerates desorption producing faster response of small response and recovery time.

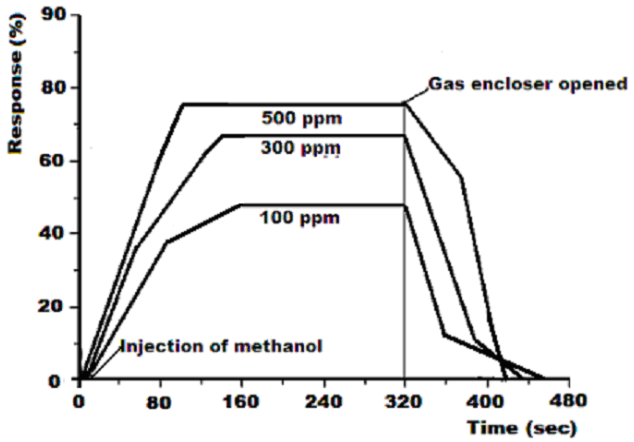

Fig 5.13 Time response characteristics of ZnO quantum dots for different concentrations of methanol at 290^0C

Table (5.5) summarizes the data of sensitivity Vs operating temperature plot and transient response at different methanol concentration

Methanol concentration (ppm)	Temperature of Maximum sensitivity (T_M)	Maximum sensitivity (%) (S_M)	Response time (Sec)	Recovery time (Sec)
100	290^0C	48	140	130
300	290^0C	67	120	90
500	290^0C	75	80	80

Table 5.5 data of sensitivity Vs operating temperature plot and transient response at different methanol concentration for ZnO/PVP sensor

5.6. Gas sensing by SnO_2 Quantum dots

5.6.1. Acetone sensing properties of SnO_2 Quantum dots Embedded in PVP matrix

To test acetone sensing, SnO_2 sample is mounted on a two-probe assembly placed in sample holder into a silica tube which is inserted coaxially inside a tubular furnace

in the similar fashion as ZnO sample. The sensing response of SnO_2 quantum dots is determined at different operating temperatures in the range 180^0C–360^0C to various concentrations of acetone [6,22] .To study sensing [1-30], at first, SnO_2 quantum dot sample is heated in a chamber in air in the absence of test gas when atmospheric oxygen is adsorbed chemically [42] on SnO_2 (as it is of n type specimen) surface. The adsorbed oxygen forms ionic species such as O^{2-}, O_2^- and O^- by the reaction kinematics as explained earlier [17] by equations (5.8), (5.9) and (5.10).

These oxygen species desorbs upon exposure to acetone vapor on SnO_2 quantum dot film (sensor in the tubular furnace) and results in decrease of SnO_2 quantum dot resistance [6,13] as acetone is reducing in nature. The desorption process occurs in the following way depending on operating temperature [14]

The reaction between acetone vapor and ionic oxygen species can take place as follow [25,36] .

$$CH_3COCH_3\ (gas) + O^- \leftrightarrow CH_3COCH_2 + OH^- + e^- \quad \ldots\ldots\ldots\ldots (5.20)$$

It is clear that acetone reacts with chemisorbed oxygen in SnO_2 quantum dot surface, inject charge carrier (e^-) to SnO_2 specimen and thereby reducing the sensor i.e quantum dot resistance. When the gas is released by opening the enclosure of the sensing chamber, the reverse process takes place and SnO_2 quantum dot resistance regains its original value.

(a) Variation of sensitivity with operating temperature

Figure 5.14 represents the response characteristics as a function of operating temperatures for three different concentrations of 100, 300 and 500 ppm of acetone vapor. At relatively low operating temperature around 180^0C, the response of SnO_2

quantum dot is restricted by slow chemical reactions (adsorption and desorption) while above 180^0C, the chemical reaction occurs very fast and efficiently resulting in higher response [4]. At 250^0C the response is maximum. This is attributed to the availability of sufficient adsorbed ionic species of oxygen on SnO_2 surface which reacts (desorbs) most effectively and rapidly with acetone molecules at this particular temperature [14] and produces large numbers of charge carriers (e^-) resulting in rapid change (decrease) in sample resistance and hence higher is the response.

At temperature higher than 250^0C, the adsorbed oxygen species available at the sensing sites on the SnO_2 quantum dot surface, are not enough to react with acetone vapor molecules[12]. This results decrease in the sensitivity. Further, it is observed that at lower concentration of acetone vapor, the sensitivity is less, while at higher concentration [12] the sensitivity is higher. This phenomenon occurs due to the fact that at lower concentration (100 ppm), the surface reaction proceeds slowly but at higher concentration (300 ppm), because of increase of surface coverage of molecules[12,42] surface reaction proceeds faster and very effectively resulting in higher sensitivity.

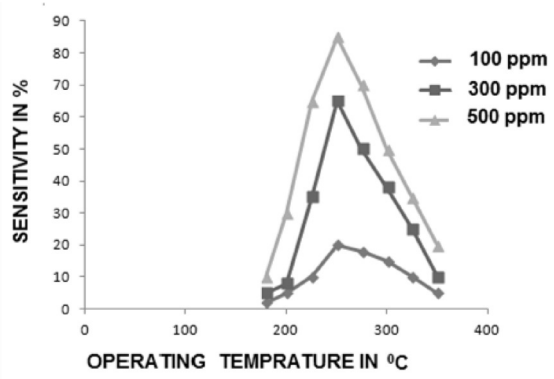

Fig 5.14: Response versus operating temperature at various concentrations of acetone vapor

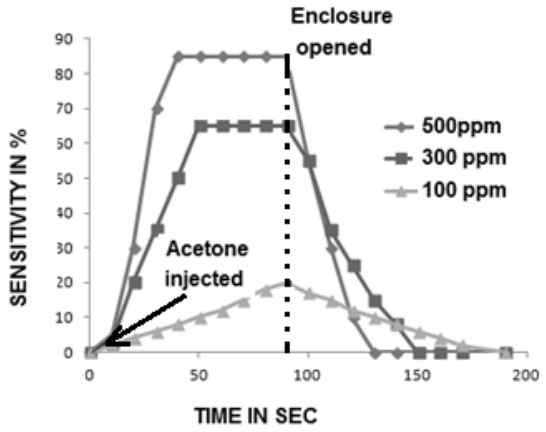

Fig 5.15: Transient response characteristics of the SnO_2 quantum dot for various acetone concentrations at 250^0C.

(b) Transient response characteristics

Figure 5.15 represents the transient response characteristics of SnO_2 quantum dot to acetone concentration of 100, 300 and 500 ppm at 250^0C. It is revealed that the response time and recovery time decrease with higher concentration. This is attributed[12] to the fact that higher concentration favors and accelerates desorption process. Response characteristic indicates that response time of SnO_2 quantum dots acetone sensor is very less (as evident from figure 5.15) which is much smaller than that of SnO_2 thin film acetone sensor[30] as well as ZnO quantum dot acetone sensor [40,41].

Table (5.6) summarizes the data of sensitivity Vs operating temperature plot and transient response at different acetone concentration.

Concentration (ppm)	Temperature of Maximum sensitivity (T_M)	Maximum sensitivity (%) (S_M)	Response time (Sec)	Recovery time (Sec)
100	250^0C	20	96	65
300	250^0C	65	46	40
500	250^0C	88	35	16

Table 5.6 data of sensitivity Vs operating temperature plot and transient response at different acetone concentration for SnO_2/PVP sensor

5.6.2. Ethanol sensing properties of SnO_2 Quantum dots Embedded in PVP matrix

To test ethanol sensing, SnO_2 sample is mounted on a two-probe assembly placed in sample holder into a silica tube which is inserted coaxially inside a tubular furnace in the similar way as explained earlier. The sensing response of SnO_2 quantum dots is determined at different operating temperatures in the range 200–400^{0}C to various concentrations of ethanol in air [8,22] .

At first [7-31], SnO_2 quantum dot sample is heated in a chamber in air in the absence of test gas when atmospheric oxygen is adsorbed chemically [22] on SnO_2 surface. The adsorbed oxygen forms ionic species such as O^{2-}, O_2^- and O^- by the reaction kinematics as explained earlier by equations (5.8), (5.9) and (5.10).

These oxygen species desorbs upon exposure to ethanol vapor and results in decrease of SnO_2 quantum dot resistance [12,13] as ethanol is reducing in nature. The desorption process occurs in the following way depending on operating temperature [36].

The reaction between ethanol vapor and ionic oxygen species can take place as follow [22,36].

$$C_2H_5OH\ (gas) + O^- \leftrightarrow CH_3CHO + H_2O + e^- \quad \ldots\ldots\ldots\ldots (5.21)$$

It is clear that ethanol reacts with chemisorbed oxygen in SnO_2 quantum dot surface, inject charge carrier (e^-) to SnO_2 specimen and thereby reducing the sensor resistance. When the gas is released by opening the enclosure of the sensing chamber, the reverse process takes place and SnO_2 quantum dot resistance regains its original value.

(a) Variation of sensitivity with operating temperature

Figure 5.16 represents the response characteristics as a function of operating temperatures for three different concentrations of 100, 300 and 500 ppm of ethanol vapor. At relatively low operating temperature around 200^0C, the response of SnO_2 quantum dot is restricted by slow chemical reaction while above 200^0C, the chemical reaction occurs very fast and efficiently resulting in higher response [13]. At 275^0C the response is maximum. This is attributed to the availability of sufficient adsorbed ionic species of oxygen on SnO_2 surface which reacts most effectively and rapidly with ethanol molecules at this particular temperature [36] and produces large numbers of charge carriers (e^-) resulting in rapid change (decrease) in sample resistance and hence higher is the response.

At temperature higher than 275^0C, the amount of adsorbed (chemisorbed) oxygen is decreased with increasing temperature, but change in surface coverage in chemisorbed oxygen becomes smaller, leading to smaller response. A decrease in intrinsic sensor resistance in air (a larger electron concentration in air) with increasing operating temperature is another reason for lower response at temperatures higher than 275ºC

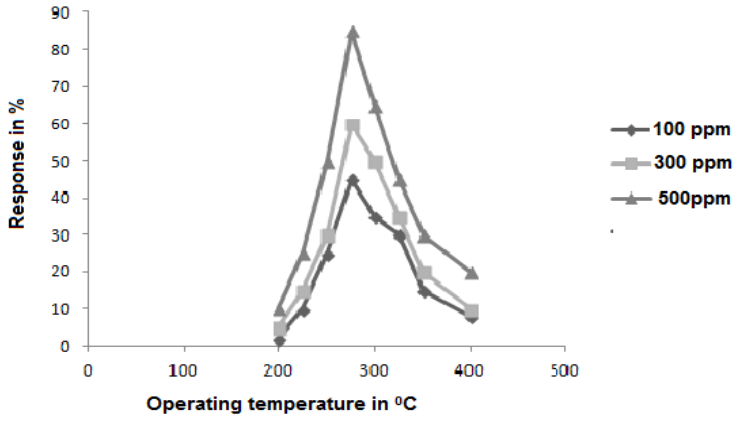

Fig 5.16:Response versus operating temperature at various concentrations of Ethanol vapour

(b) Transient response characteristics

Figure 5.17 represents the transient response characteristics of SnO_2 quantum dot to ethanol concentration of 100, 300 and 500 ppm at 275^0C. Examining the graphs, it is revealed that the response time and recovery time decrease with higher concentration. This is attributed [13] to the fact that higher concentration favors and accelerates the desorption resulting in small response and recovery time.

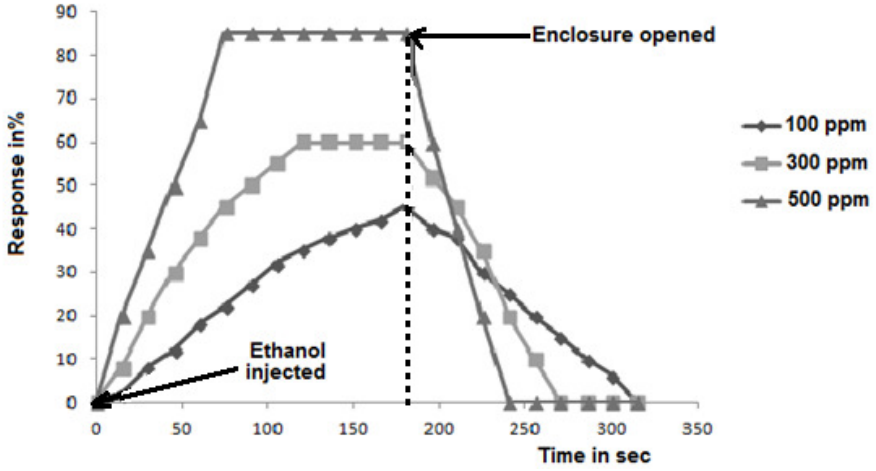

Fig 5.17 : Transient response characteristics of the Sno2 quantum dot for various Ethanol concentrations at 275^0C

Transient response characteristic indicates that response time of SnO_2 quantum dots ethanol sensor is very less (as evident from figure 5.17) which is much smaller than that of SnO_2 thin film ethanol sensor[22].

Table (5.7) summarizes the data of sensitivity Vs operating temperature plot and transient response at different ethanol concentration.

Concentration (ppm)	Temperature of Maximum sensitivity (T_M)	Maximum sensitivity (%) (S_M)	Response time(Sec)	Recovery time (Sec)
100	275^0C	45	150	110
300	275^0C	60	100	70
555500	275^0C	85	50	50

Table 5.7 : Data of sensitivity Vs operating temperature plot and transient response at different ethanol concentration for SnO_2/PVP sensor

5.6.3 Methanol sensing properties of SnO_2 Quantum dots Embedded in PVP matrix.

Methanol sensing

To test methanol sensing[8,12] SnO_2 quantum dot sample is mounted on a two-probe assembly placed in sample holder into a silica tube in the similar way explained earlier. At first, SnO_2 quantum dot sample is heated in the chamber in air in absence of methanol vapor, and atmospheric oxygen is adsorbed chemically on SnO_2 surface. The adsorbed oxygen forms ionic species such as O2-, O2- and O- by the reaction kinematics as explained earlier by equations (5.8),(5.9) & (5.10)[15] Next, these oxygen species desorbs upon exposure to methanol vapor (gas) and results in decrease of SnO_2 quantum dot resistance [8,14,27] . The desorption occurs in one of the following two ways depending on operating temperature [8]

CH3OH + O−(adsorbed) _ HCOH + H2O + e−…….(5.22)

CH3OH+ O2−(adsorbed)_ HCOOH + H2O + e−……..(5.23)

It is evident from equation (5.22) and (5.23) that methanol was oxidized to formic acid, and liberated electrons on SnO_2 surface, thereby decreasing its resistance.

When the gas is released by opening the enclosure of the sensing chamber, the reverse process is taken place and specimen (quantum dot) resistance regains its original value.

(a) Variation of sensitivity with operating temperature

Figure 5.18 represents the response characteristics as a function of operating temperatures for three different concentrations of 100, 300 and 500 ppm of methanol vapor. At relatively low operating temperature around 170^0C, the response of SnO_2 quantum dot is restricted by slow chemical reaction (adsorption and desorption) while above 170^0C, the reaction occurs very fast and efficiently resulting in higher response[8]. At 250^0C the sensitivity is maximum. This is attributed to the availability of sufficient adsorbed ionic species of oxygen on SnO_2 surface which reacts most effectively and rapidly with methanol molecules at this temperature [6,8] and produces large numbers of charge carriers (e-) resulting in rapid change (decrease) in sample resistance and hence results higher response.

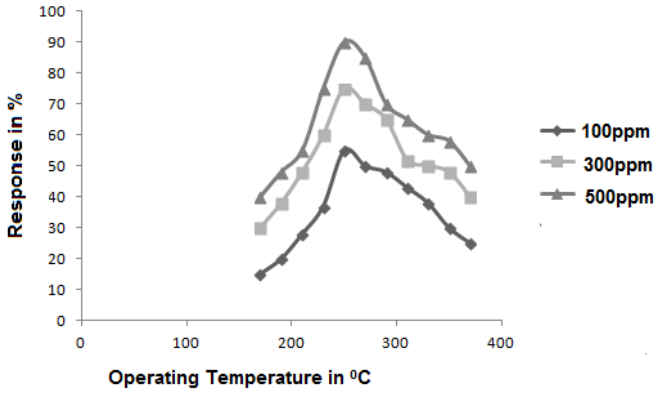

Fig 5.18 Response Vs operating temperature for different methanol concentrations for SnO_2 sensor

(b) Transient response characteristics

Figure 5.19 represents the transient response characteristics of SnO_2 quantum dots to methanol concentrations of 100, 300 and 500 ppm at 250^0C. Examining the graphs, it is revealed that response time and recovery time decreases with higher concentration. This is attributed [8,23] to the fact that higher concentration favors and accelerates the desorption of the reaction products. The response characteristics indicate that response time &recovery time of SnO_2 quantum dots methanol sensor is less (as evident from Figure 5.19) which is much smaller than that of ZnO and Fe_2O_3 [31,32,] quantum dot methanol sensor.

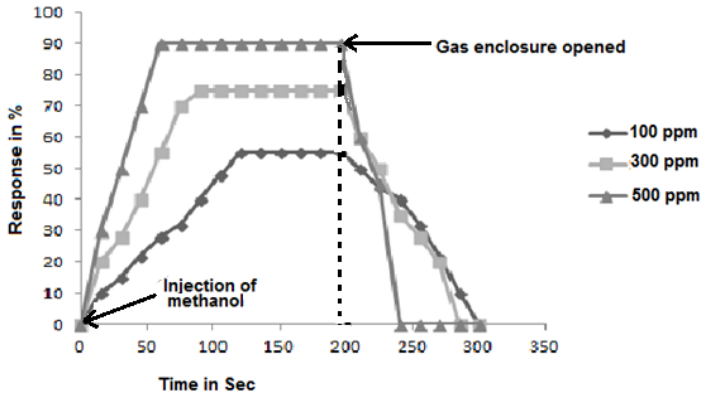

Figure 5.19 Time response characteristics of SnO_2 quantum dots for different concentrations of methanol at 250^0C

Table (5.8) summarizes the data of sensitivity Vs operating temperature plot and transient response at different methanol concentration..

Concentration (ppm)	Temperature of Maximum sensitivity (T_M)	Maximum sensitivity (%) (S_M)	Response time (Sec)	Recovery time(Sec)
100	250^0C	53	100	100
300	250^0C	77	66	70
500	250^0C	90	45	40

Table 5.8: data of sensitivity Vs operating temperature plot and transient response at different methanol concentration for SnO_2/PVP sensor

5.7 Gas sensing by Fe_2O_3 Quantum dots films

5.7.1 Acetone sensing properties of Fe_2O_3 Quantum dots Embedded in PVP matrix

To test acetone sensing, Fe_2O_3 quantum dots sample is mounted on a two-probe assembly placed in sample holder into a silica tube which is inserted coaxially inside a tubular furnace in the similar fashion as ZnO & SnO_2 sample. The sensing response of Fe_2O_3 quantum dots is determined at different operating temperatures in the range 180^0C–380^0C to various concentrations of acetone[16,17,35]. To study sensing [5-42], at first, Fe_2O_3 quantum dot sample is heated in a chamber in air in the absence of test gas when atmospheric oxygen is adsorbed chemically [17] on Fe_2O_3 (as it is of n type specimen) surface. The adsorbed oxygen forms ionic species such as O^{2-}, O_2^- and O^- by the reaction kinematics as explained earlier [17] by equations (5.8), (5.9) and (5.10).

These oxygen species desorbs upon exposure to acetone vapor on Fe_2O_3 quantum dot film (sensor in the tubular furnace) and results in decrease of Fe_2O_3 quantum dot resistance [5,32] as acetone is reducing in nature. The desorption process occurs in the following way depending on operating temperature [17]

The reaction between acetone vapor and ionic oxygen species can take place as follow [30,35]

$$CH_3COCH_3\ (gas) + O^- \leftrightarrow CH_3COCH_2 + OH^- + e^- \ldots\ldots\ldots \quad (5.24)$$

It is clear that acetone reacts with chemisorbed oxygen in Fe_2O_3 quantum dot surface, inject charge carrier (e^-) to Fe_2O_3 specimen and thereby reducing the sensor i.e quantum dot resistance. When the gas is released by opening the enclosure of the

sensing chamber, the reverse process takes place and Fe_2O_3 quantum dot resistance regains its original value.

(a) Variation of sensitivity with operating temperature

Figure 5.20 represents the response characteristics as a function of operating temperatures for three different concentrations of 100, 300 and 500 ppm of acetone vapor. At relatively low operating temperature around 180^0C, the response of Fe_2O_3 quantum dot is restricted by slow chemical reactions (adsorption and desorption) while above 180^0C, the chemical reaction occurs very fast and efficiently resulting in higher response [16]. At 300^0C the response is maximum. This is attributed to the availability of sufficient adsorbed ionic species of oxygen on Fe_2O_3 surface which reacts (desorbs) most effectively and rapidly with acetone molecules at this particular temperature[18] and produces large numbers of charge carriers (e^-) resulting in rapid change (decrease) in sample resistance and hence higher is the response.

At temperature higher than 300^0C, the adsorbed oxygen species available at the sensing sites on the Fe_2O_3 quantum dot surface, are not enough to react with acetone vapor molecules [18].This results decrease in the sensitivity. Further, it is observed that at lower concentration of acetone vapor, the sensitivity is less, while at higher concentration [17] the sensitivity is higher. This phenomenon occurs due to the fact that at lower concentration (100 ppm), the surface reaction proceeds slowly but at higher concentration (300 ppm), because of increase of surface coverage of molecules [17,33] surface reaction proceeds faster and very effectively resulting in higher sensitivity.

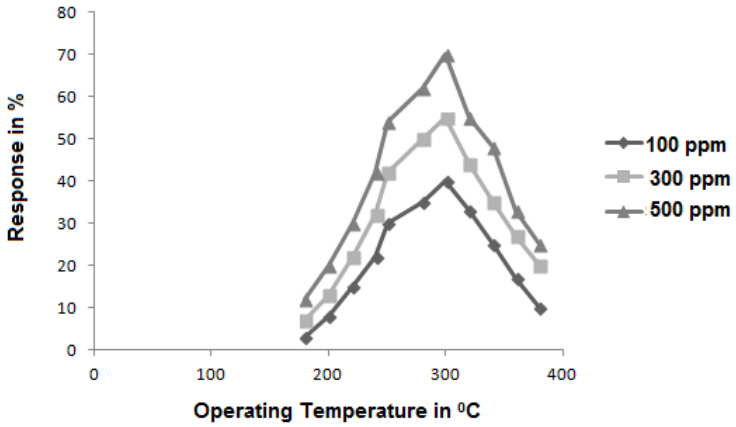

Fig 5.20: Response versus operating temperature at various concentrations of acetone vapor

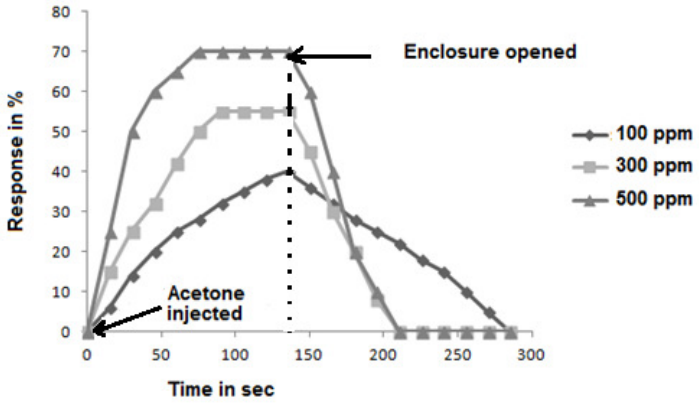

Fig 5.21: Transient response characteristics of the Fe_2O_3 quantum dot for various acetone concentrations at 300^0C

(b) Transient response characteristics

Figure 5.21 represents the transient response characteristics of Fe_2O_3 quantum dot to acetone concentration of 100, 300 and 500 ppm at 300^0C. It is revealed that the response time and recovery time decrease with higher concentration. This is attributed[17,32] to the fact that higher concentration favors and accelerates desorption process. Response characteristic indicates that response time of Fe_2O_3 quantum dots acetone sensor is very less (as evident from figure 5.21)

Table (5.9) summarizes the data of sensitivity Vs operating temperature plot and transient response at different acetone concentration.

.Concentration (ppm)	Temperature of Maximum sensitivity (T_M)	Maximum sensitivity (%) (S_M)	Response time (Sec)	Recovery time (Sec)
100	300^0C	40	110	120
300	300^0C	55	70	43
500	300^0C	70	50	40

Table 5.9: Data of sensitivity Vs operating temperature plot and transient response at different acetone concentration for Fe_2O_3/PVP sensor

5.7.2 Ethanol sensing properties of Fe_2O_3 Quantum dots Embedded in PVP matrix

To test ethanol sensing [1-42], Fe_2O_3 sample is mounted on a two-probe assembly placed in sample holder into a silica tube which is inserted coaxially inside a tubular furnace in the similar way as explained earlier. The sensing response of Fe_2O_3 quantum dots is determined at different operating temperatures in the range 200–350^0C to various concentrations of ethanol in air [21,23] .

At first [5-42], Fe_2O_3 quantum dot sample is heated in a chamber in air in the absence of test gas when atmospheric oxygen is adsorbed chemically [13] on Fe_2O_3 (as it is of n-type specimen) surface. The adsorbed oxygen forms ionic species such as O^{2-}, O_2^- and O^- by the reaction kinematics as explained earlier by equations (5.8),(5.9) and (5.10).

These oxygen species desorbs upon exposure to ethanol vapor and results in decrease of Fe_2O_3 quantum dot resistance [11,33] as ethanol is reducing in nature. The

desorption process occurs in the following way depending on operating temperature [23].

The reaction between ethanol vapor and ionic oxygen species can take place as follow [23,28] .

$$C_2H_5OH\ (gas) + O^- \leftrightarrow CH_3CHO + H_2O + e^- \quad \text{.....(5.25)}$$

It is clear that ethanol reacts with chemisorbed oxygen in Fe_2O_3 quantum dot surface, inject charge carrier (e^-) to Fe_2O_3 specimen and thereby reducing the sensor resistance. When the gas is released by opening the enclosure of the sensing chamber, the reverse process takes place and Fe_2O_3 quantum dot resistance regains its original value.

(a) Variation of sensitivity with operating temperature

Figure 5.22 represents the response characteristics as a function of operating temperatures for three different concentrations of 100, 300 and 500 ppm of ethanol vapor. At relatively low operating temperature around 200^0C, the response of Fe_2O_3 quantum dot is restricted by slow chemical reaction while above 200^0C, the chemical reaction occurs very fast and efficiently resulting in higher response [32]. At 290^0C the response is maximum. This is attributed to the availability of sufficient adsorbed ionic species of oxygen on Fe_2O_3 surface which reacts most effectively and rapidly with ethanol molecules at this particular temperature [13] and produces large numbers of charge carriers (e^-) resulting in rapid change (decrease) in sample resistance and hence higher is the response.

At temperature higher than 290^0C, the amount of adsorbed (chemisorbed) oxygen is decreased with increasing temperature, but change in surface coverage in

chemisorbed oxygen becomes smaller, leading to smaller response. A decrease in intrinsic sensor resistance in air (a larger electron concentration in air) with increasing operating temperature is another reason for lower response at temperatures higher than 290ºC .

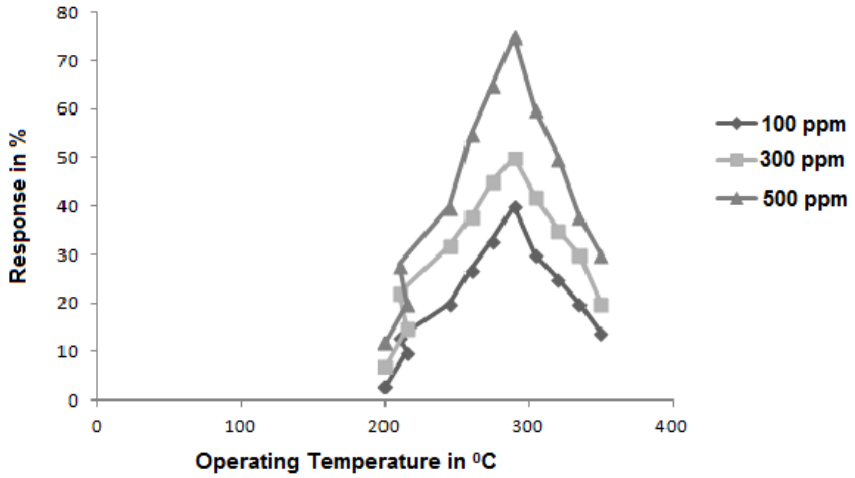

Fig 5.22: Response versus operating temperature at various concentrations of ethanol vapour

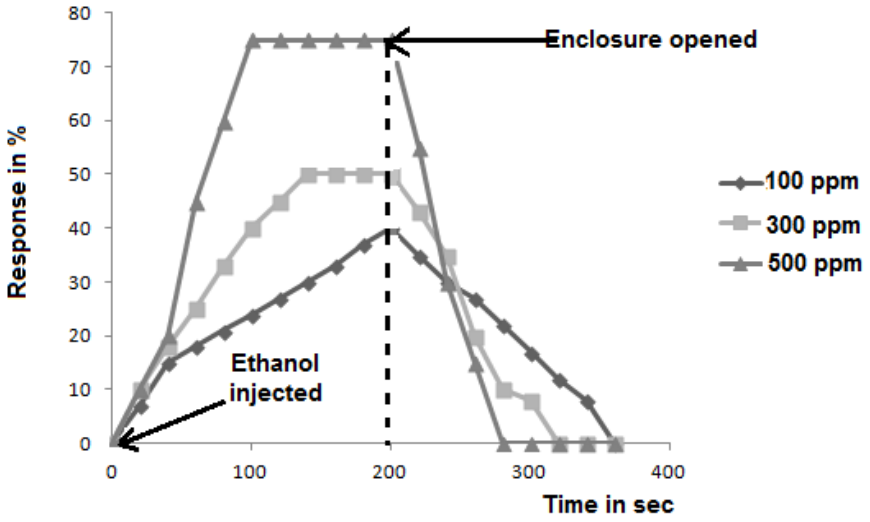

Fig 5.23: Transient response characteristics of the Fe_2O_3 quantum dot for various Ethanol concentration at 290^0C

(b) Transient response characteristics

Figure 5.23 represents the transient response characteristics of Fe_2O_3 quantum dot to ethanol concentration of 100, 300 and 500 ppm at 290^0C. Examining the graphs, it is revealed that the response time and recovery time decrease with higher concentration. This is attributed [13] to the fact that higher concentration favors and accelerates the desorption resulting in small response and recovery time.

Transient response characteristic indicates that response time & recovery time of Fe_2O_3 quantum dots ethanol sensor is very less (as evident from figure 5.23).

Table (5.10) summarizes the data of sensitivity Vs operating temperature plot and transient response at different ethanol concentration.

Concentration (ppm)	Temperature of Maximum sensitivity (T_M)	Maximum sensitivity (%) (S_M)	Response time (Sec)	Recovery time(Sec)
100	290^0C	40	162	150
300	290^0C	50	124	100
500	290^0C	75	85	80

Table 5.10: Data of sensitivity Vs operating temperature plot and transient response at different ethanol concentration for Fe_2O_3/PVP sensor

5.7.3 Methanol sensing properties of Fe_2O_3 quantum dots Embedded in PVP matrix.

To test methanol sensing [1-42] Fe_2O_3 quantum dot sample is mounted on a two-probe assembly placed in sample holder into a silica tube in the similar way explained earlier. At first, Fe_2O_3 quantum dot sample is heated in the chamber in air in

absence of methanol vapor, and atmospheric oxygen is adsorbed chemically on Fe_2O_3 surface. The adsorbed oxygen forms ionic species such as O2-, O2- and O- by the reaction kinematics as explained earlier by equations (5.8),(5.9)&(5.10). [33] Next, these oxygen species desorbs upon exposure to methanol vapor (gas) and results in decrease of Fe_2O_3 quantum dot resistance [28,33,35] (as methanol is reducing in nature) . The desorption occurs in one of the following two ways depending on operating temperature [39]

CH3OH + O−(adsorbed) _ HCOH + H2O + e−…….(5.26)

CH3OH+ O2−(adsorbed)_ HCOOH + H2O + e−……..(5.27)

It is evident from equation (5.26) and (5.27) that methanol was oxidized to formic acid, and liberated electrons on Fe_2O_3 surface, thereby decreasing its resistance. When the gas is released by opening the enclosure of the sensing chamber, the reverse process is taken place and specimen (quantum dot) resistance regains its original value.

(a) Variation of sensitivity with operating temperature

Figure 5.24 represents the response characteristics as a function of operating temperatures for three different concentrations of 100, 300 and 500 ppm of methanol vapor. At relatively low operating temperature around 180^0C, the response of Fe_2O_3 quantum dot is restricted by slow chemical reaction (adsorption and desorption) while above 180^0C, the reaction occurs very fast and efficiently resulting in higher response [10]. At 300^0C the sensitivity is maximum. This is attributed to the availability of sufficient adsorbed ionic species of oxygen on Fe_2O_3 surface which reacts most effectively and rapidly with methanol molecules at this temperature [8,10]

and produces large numbers of charge carriers (e-) resulting in rapid change (decrease) in sample resistance and hence higher response. At temperature higher than 300^0C, the amount of adsorbed (chemisorbed) oxygen is decreased with increasing temperature, leading to smaller response.

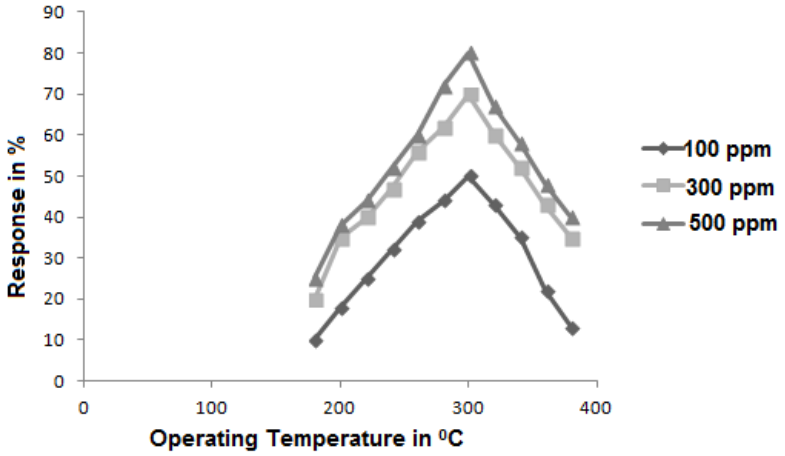

Fig5.24 : Response Vs operating temperature for different methanol concentrations for Fe_2O_3 sensor

(b) Transient response characteristics

Figure 5.25 represents the transient response characteristics of Fe_2O_3 quantum dots to methanol concentrations of 100, 300 and 500 ppm at 300^0C. Examining the graphs, it is revealed that response time and recovery time decreases with higher concentration. This is attributed [33,39] to the fact that higher concentration favors and accelerates the desorption of the reaction products. The response characteristics indicate that response time and recovery time of Fe_2O_3 quantum dots is less (as evident from Figure 5.25) which is much smaller than that of ZnO quantum dot methanol sensor[31,32].

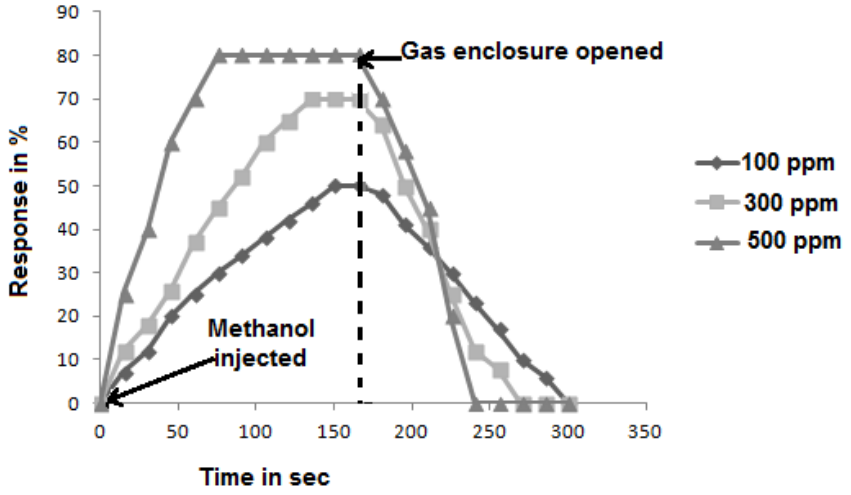

Figure 5.25 Time response characteristics of Fe_2O_3 quantum dots for different concentrations of methanol at 300^0C

Table (5.11) summarizes the data of sensitivity Vs operating temperature plot and transient response at different methanol concentration.

Concentration (ppm)	Temperature of Maximum sensitivity (T_M)	Maximum sensitivity (%) (S_M)	Response time (Sec)	Recovery time (Sec)
100	300^0C	50	138	110
300	300^0C	70	110	80
500	300^0C	80	50	55

Table5.11: data of sensitivity Vs operating temperature plot and transient response at different methanol concentration for Fe_2O_3/PVP sensor

5.8 Conclusion: The prepared quantum dots samples namely ZnO, SnO_2 and Fe_2O_3 have been tested for their applications for sensing of three reducing gases acetone, ethanol and methanol. ZnO quantum dots (embedded in PVP) acetone sensor has higher sensitivity in compare to that of ZnO (embedded on PVA), Fe_2O quantum

dots (embedded in PVP) acetone sensor and is comparable to that of SnO_2 quantum dots (embedded in PVP) acetone sensor. Response time & Recovery time is less for SnO2/PVP quantum dots acetone sensor as compared to ZnO/PVP quantum dots acetone sensor and the Fe_2O_3/PVP quantum dots acetone sensor. SnO_2/PVP quantum dots Ethanol sensor has higher sensitivity, as compared to ZnO/PVP quantum dot Ethanol sensor and the Fe_2O_3 /PVP quantum dots Ethanol sensor. But response time & recovery time are less for ZnO/PVP ethanol sensor as compared to SnO_2/PVP ethanol sensor& Fe_2O_3 /PVP ethanol sensor. SnO_2/PVP quantum dots methanol sensor has higher sensitivity, less response & recovery time as compared to the ZnO/PVP quantum dots methanol sensor and the Fe_2O_3 /PVP quantum dots methanol sensor.

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