



Study of Synthesis of Zinc Oxide (ZnO) Quantum Dot And its Application as a Gas Sensor

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Abstract: -

In this paper, we have presented a basic analysis of Zinc Oxide (ZnO) Quantum Dot Gas Sensor. We have studied the synthesis of Zinc Oxide (ZnO) quantum dots embedded in polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) matrix. The sensor response has been measured for different pollutant gases including acetone (C₃H₆O) and ethanol (C₂H₅OH) for different concentrations in the 100ppm-500ppm range. We have studied sensitivity and transient characteristics of Acetone(C₃H₆O) and Ethanol (C₂H₆) reducing vapors via Zinc Oxide (ZnO) Quantum Dot Gas Sensor embedded in PVP and PVA matrix. The samples have been prepared via quenching technique where bulk Zinc Oxide (ZnO) powder is calcined at a very high temperature of 1200°C and then quenched into ice cold polyvinylpyrrolidone solution. For the synthesis of Zinc Oxide (ZnO) Quantum Dot embedded in PVA matrix, we use Zinc Oxide (ZnO) powder is calcined at very high temperature of 1000°C and then quenched into ice cold polyvinyl alcohol (PVA) solution. We have studied this sample's specimen characteristics by using Optical analysis such as UV-VIS spectroscopy, which ranged from the ultraviolet (UV) region to the near-infrared (NIR) region.

Keywords:- Quantum Dot (QD), Zinc Oxide(ZnO), PVP(polyvinylpyrrolidone), PVA(polyvinyl alcohol), Gas Sensor, Acetone(C₃H₆O), Ethanol(C₂H₅OH)

1. Introduction: -

Modern research has made it possible to design and fabricate semiconductor nanoparticles, especially those belonging to the II-VI, III- V and IV- V groups of the periodic table. These semiconductors exhibit considerable quantum size dependent electronic and optoelectronic devices [1-2].

A quantum dot (QD) is a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes, or excitons (bound pairs of conduction band electrons and valence band holes) in all three spatial directions. If all the three dimensions, that is thickness, width and length of any structure are comparable to de-Broglie's wavelength of electrons at Fermi energy and the electronic motion is restricted

in all the three dimensions, the structure is called quantum dot. Practically, its dimensions range from a few nm to a few hundred nm that are circular, elliptical or rectangular in shape.

These are the particles that carry the electricity, and because of this confinement, the quantum dot has a distinct energy level [3]. It is ideally a quasi-zero structure. A quantum dot is a nanometre-sized crystal of inorganic semiconductor, or semiconductor nanocrystal. It has the same arrangement of atoms as in the corresponding bulk material, but many more surface atoms due to three-dimensional confinement. Due to high surface-to-volume (S/V) ratio of Quantum dots and well-organized molecular structure, and single crystalline make Quantum Dots nanostructures unique and prominent candidates for gas sensing application [6]. Gas attachment sensing mechanisms, such as O^- , O_2 , H^+ , and OH^- contact as analytes that result in change in the electrical conductivity of the charges, is mainly dependent on the redox reaction.

In the present paper, we have analyzed Zinc Oxide (ZnO) Quantum Dot which is highly sensitive to reducing and oxidizing gases. It is easier and cheaper to fabricate metal oxide semiconductor quantum dots. Unlike in bulk material, electronic transition between traps and valence band as well as traps and conduction band are faster due to fast trapping and de-trapping of charge carriers by traps than band edge transition. This property of quantum dots makes it efficient for faster response [4-5].

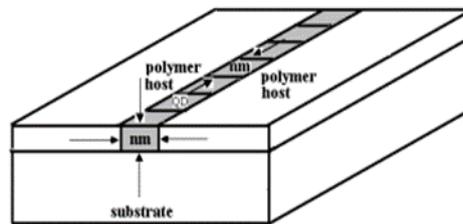


Fig-1 Quantum Dot

2. Theoretical Description: -

2.1 Zero-Dimensional Structures: Quantum Dots and Nanodots

The cuboid quantum dot, more often designated as the quantum box shown in Fig.3.1 This special case can be used for a qualitative description of the response of quantum dots of many shapes. Zero dimensional structures of other shapes, such as spherical quantum dots require a numerical solution of the Schrödinger equation. The quantum box is a generalization of a quantum wire of rectangular cross-section, in that there is additional confinement along the x axis to $0 < x < L_x$. This additional confinement removes the only degree of freedom remaining in the particle's momentum, thus localizing it in all three directions. According to the Heisenberg uncertainty principle, increased spatial confinement will result in increased energy of the confined states.

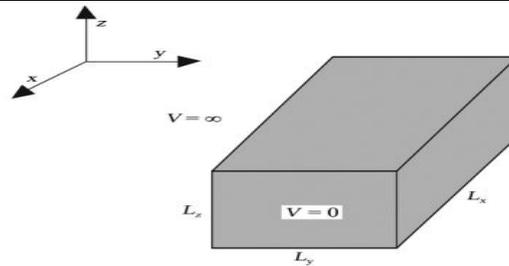


Fig 3.1. The cuboid Quantum dot

For simplicity, let the potential be zero inside the quantum box but infinite everywhere else; i.e.,

$$V = (x, y, z) \begin{cases} 0, & \{0 < x < L_x\} \cap \{0 < y < L_y\} \cap \{0 < z < L_z\} \\ \infty, & \text{otherwise} \end{cases} \quad (1)$$

The 3D time-harmonic Schrödinger equation within the quantum box becomes

$$-\frac{\hbar}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \varphi(x, y, z) = E\varphi(x, y, z) \quad (2)$$

The method of separation of variables applies, leading to Eigen functions described by three principal quantum numbers (n_x, n_y, n_z) as follows:

$$\varphi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin \sin \left(\frac{n_x \pi x}{L_x} \right) \sin \sin \left(\frac{n_y \pi y}{L_y} \right) \sin \sin \left(\frac{n_z \pi z}{L_z} \right), \quad (3)$$

$$n_x = 1, 2, 3, \dots, n_y = 1, 2, 3, \dots, n_z = 1, 2, 3, \dots$$

The Eigen energy for a specific Eigen function is given by

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad (4)$$

$$n_x = 1, 2, 3, \dots, n_y = 1, 2, 3, \dots, n_z = 1, 2, 3, \dots$$

Of fundamental importance is the fact that E_{n_x, n_y, n_z} is the total particle energy because of 3D confinement,

The discrete energy spectrum in a quantum box and the lack of free propagation are the main features distinguishing quantum dots from quantum wells and quantum wires. As these features are typical for atoms, quantum dots and quantum boxes are often called artificial atoms.

2.2 Synthesis of Zinc Oxide (ZnO) Quantum Dot by Quenching Method

In the quenching method, the bulk powder of the specimen is sintered in a furnace at very high temperature for a long time and then it is immediately put into a polymer matrix, kept at ice cold condition followed by its moderate stirring. Sudden cooling of very hot (about 1000°C) semiconductor material causes its fragmentation, and produces quantum dot nanoparticles. These nanoparticles enter into the gaps of the matrix and produce stable quantum dots. In the quenching method, size of quantum the dot can be controlled by varying Sintering temperature, Sintering period and Temperature of matrix during quenching [8-9].

2.2.1 Synthesis of ZnO quantum dots on polyvinylpyrrolidone (PVP) matrix

To synthesize Zinc Oxide (ZnO) quantum dots by quenching method, 3 gm of Zinc Oxide (ZnO) powder (99.99% pure, E Merck) is calcined at $\sim 1200^{\circ}\text{C}$ for 10 hours and then quenched into 4 wt.% aqueous solution of polyvinylpyrrolidone (PVP) matrix (99.9% pure, E Merck) kept at ice cold temperature followed by its moderate stirring (~ 175 rpm) for 30 minutes [10]. This solution contains ZnO quantum dots embedded in polyvinylpyrrolidone.

2.2.2 Synthesis of ZnO quantum dots on Polyvinyl Alcohol (PVA) matrix

To synthesize ZnO/PVA quantum dots by quenching method, 2 gm of bulk Zinc Oxide (ZnO) powder is kept in the furnace for sintering at 1000°C for 5 hours. After sintering, the sample is taken out of the furnace very carefully and immediately put into a 6wt% ice cold aqueous solution of PVA followed by its moderate stirring in room temperature for half an hour [4]. After stabilizing the solution (by keeping it in a dark chamber for 5 hours) it is cast over glass substrate and then dried in the oven. This solution contains Zinc Oxide (ZnO) quantum dots embedded in polyvinyl alcohol [8-9].

2.3 Characterization of Zinc Oxide (ZnO) Quantum Dot by UV-Visible spectroscopy

Ultraviolet-visible (UV-VIS) spectroscopy involves the spectroscopy of photons in the UV-visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy [11]. Fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

The instrument used in ultraviolet-visible spectroscopy is called a UV-VIS spectrophotometer. It measures the intensity (I) of light passing through a sample and compares it to the intensity (I_0) of light before it passes through the sample. The ratio (I/I_0) is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A is based on the transmittance as

$$A = -\log (T\%) \quad (5)$$

Optical absorbance (A) is an important way to explore the different energy states in semiconductor material [12]. This study is based on the fact that, if two possible energy states E_1 and E_2 exist in a system as shown in Figure 3.2, then electronic transition from level E_1 to E_2 can take place when appropriate energy $E_2 - E_1 = \Delta E$ is absorbed and the frequency of radiation has the simple form of

$$\nu = \frac{\Delta E}{h} \text{ Hz} \quad (6)$$

or $\Delta E = h\nu$ joules

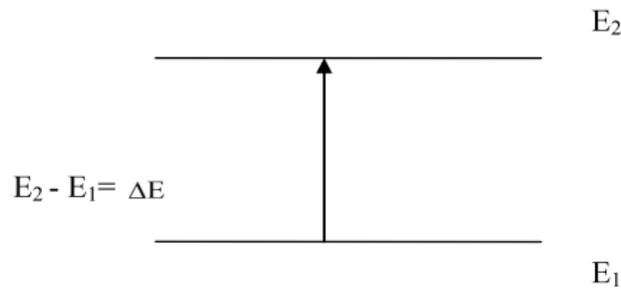


Fig Fig.-2.2 electronic excitation

That is, absorption wavelength or edge can be written as

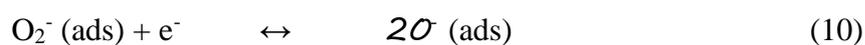
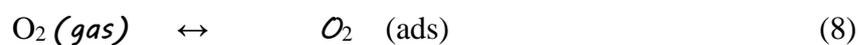
$$\lambda_a = \frac{hc}{\Delta E} \quad (9)$$

Where ' λ_a ' is the absorption edge, 'h' is Planck's constant and 'c' is the velocity of light.

2.4 Sensing mechanism of metal oxide Zinc Oxide (ZnO) semiconductor gas sensors

A Gas sensor is a component that converts the presence of a gas or vapor into an electrically measurable signal [12]. It is well known that the resistance of a 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/vapor [13-14].

2.4.1 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 [16]. Adsorption is temperature dependent. It is also material dependent and hence it is not same for all types of sensor materials. Adsorption takes place by the following equations:



The formation of O_2^- species is also possible as follows



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

2.4.2 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 [16]. During desorption, reducing gas acting on the oxide's sensor surface undergoes the following reaction.



Where R is the reducing gas, e^- are electrons injected to the sensor surface (conduction band). Both adsorption and desorption are material dependent properties.

2.4.3 Response: The response (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 [17].

$$S = \frac{\Delta R}{R} \quad (13)$$

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

$$S = \left(\frac{R_a - R_g}{R_a} \right) \times 100\% \quad (14)$$

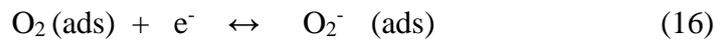
Where, R_a = resistance of quantum dot film in air, R_g = resistance of quantum dot film upon exposure to gas /vapor. Every time prior to exposing the quantum dots (quantum dot film) to the test gas/ vapor, it has been allowed to equilibrate inside the gas chamber at operating temperature for 30 minute and the stabilized resistance is taken as R_a [18]. Sensitivity varies with two parameters operating temperature concentration of gas or vapor [19-10].

2.4.4 Response time (T_{res}) And Recovery time (T_{rec}): 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. 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 [21].

2.5 Acetone sensing properties of Zinc Oxide (ZnO) Quantum dots embedded in Polyvinyl Alcohol (PVA) matrix

To study sensing of acetone (test gas), at first, ZnO quantum dot sample is heated in a chamber in air in the absence of test gas when atmospheric oxygen is absorbed chemically on the ZnO on (as it is of n type

specimen) surface [24-25]. The absorbed oxygen formed ionic species such as O^{2-} , O^- and O_2^- by the following reaction kinematics given below [22-23].



The formation of O_2^- species is also possible as follows



These oxygen species desorb upon exposure to acetone vapor (gas) and result in decrease of ZnO quantum dot resistance as acetone is reduced in nature. The desorption process occurs in one of the following ways depending on operating temperature [10].



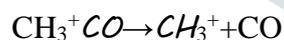
$$k = 1.0 \times 10^{12} e^{(-21000/RT)} [cm^3/mols]$$



$$k = 2.0 \times 10^{12} e^{(-63,000/RT)} [cm^3/mols]$$



$$k = 1.0 \times 10^{12} e^{(-42,000/RT)} [cm^3/mols] \quad (22)$$



$$k = 2.0 \times 10^{11} e^{(-15,000/RT)} [1/s] \quad (23)$$

It is clear that in both the cases Equation (20) (21) and (23) acetone reacts with chemisorbed oxygen in ZnO quantum dot surface, inject charge carrier (e^-) to ZnO specimen and thereby reducing the sensor resistance.

2.6 Ethanol sensing properties of Zinc Oxide (ZnO) Quantum dots Embedded in PVP matrix.

To test ethanol sensing, a Zinc Oxide (ZnO) sample is mounted on a two-probe assembly placed in a 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 quantum dots is

determined at different operating temperatures in the range 220-360°C to various concentrations of ethanol. To study sensing at first, the ZnO quantum dot sample is heated in a chamber in air in the absence of test vapor when atmospheric oxygen is adsorbed chemically on the ZnO surface [15-17]. The adsorbed oxygen forms ionic species such as O^{2-} , O_2^- and O^- by the reaction kinematics already explained. These oxygen species desorb upon exposure to ethanol and results in decrease of ZnO quantum dot resistance as ethanol is reducing in, all, ' nature. The desorption process occurs in the following way



3. Results and discussion: -

3.1 Variation of sensitivity of Acetone with operating temperature embedded in PVA matrix

It is observed that at lower concentration of acetone vapor, the sensitivity is less, while at higher concentration the sensitivity is high. This phenomenon occurs due to the fact that at lower concentration (100 ppm), the surface reaction proceeds slowly as there is few molecules of acetone react with oxygen species as a result number of charge carrier reduces due to this sensitivity also reduces, but at higher concentration (300 ppm, 500 ppm), because of increase of surface coverage of molecules 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 12% to 21 % as the temperature is raised from 220°C to 300° C and then decreases to 7 % when the temperature is further raised to 360° C. In this case the optimum operating temperature is 300° C at which the sensitivity is found to be maximum for each concentration of acetone. The quantum dots show a maximum sensitivity of 69% for 500 ppm of acetone at 300°C.

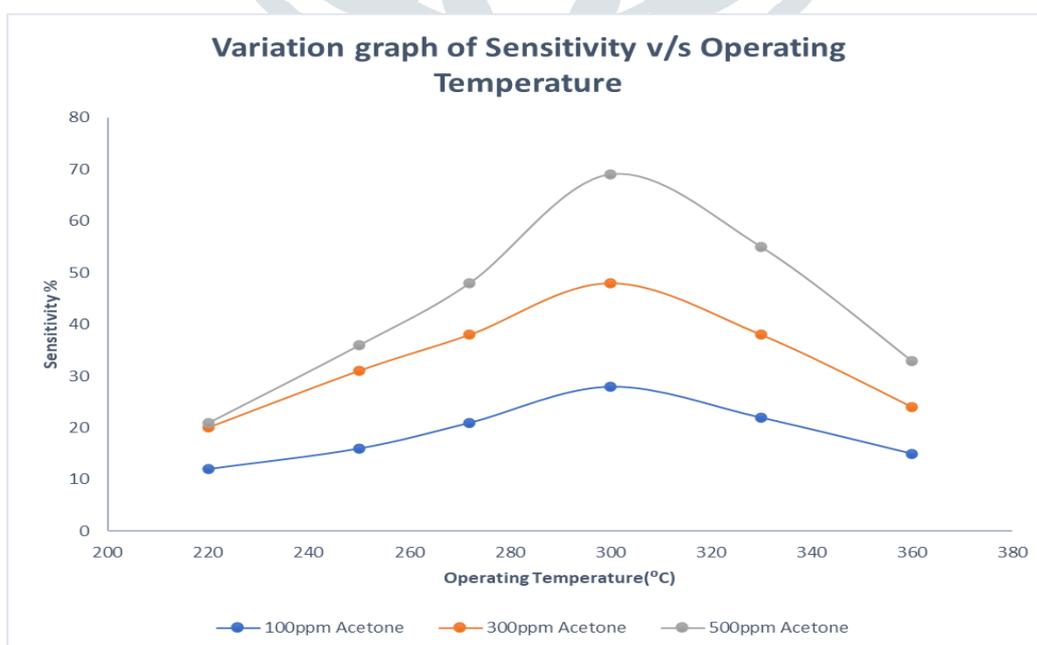


Fig 3.1 Acetone sensing with operating temperature embedded in PVA

Matrix

At relatively low operating temperature of 220°C, the nature of sensitivity of the quantum dot sensor is restricted or not changes suddenly because of there is resistance offered by bulk of individual grain to electron flow or the nature of chemical reaction such as Adsorption and Desorption process which is does not takes place rapidly in the case of low temperature. When the sensor is heated above 220°C, the adsorbed oxygen species react with reducing gases and chemical reaction occurs very fast and effectively as a result electrons are injected into Quantum dot ZnO semiconductor due to this flow of electrons increases and its resistivity decreases. These results increase in its sensitivity. At a temperature of 300°C, at high temperature sensitivity of the sample is maximum. This takes place due to high desorption i.e., at high temperature desorption takes place, this leads to rapid chemical reaction between acetone molecule and adsorbed oxygen species which is available on ZnO quantum dot film surface. This reaction between Acetone molecules and Oxygen species generates large numbers of charge carriers (e^-) resulting in decrease in sensor resistance and hence higher is the response or sensitivity. At higher temperature above 300°C, the adsorbed oxygen species available at the sensing sites on the quantum dot surface, are not enough to react with acetone vapor molecules due to higher thermal/kinetic energy imparted to the gas molecule thus reducing the gas reaction i.e. there is very few oxygen species to react with acetone vapor as a result injection of electron does not takes place due to this resistance of quantum dot gas sensor increases this phenomenon leads to decrease in sensitivity of ZnO QDs gas sensor.

3.2 Transient response characteristics or Variation of Sensitivity with operating time of acetone with ZnO embedded in PVA matrix

Transient response characteristic indicates that response time and recovery time of ZnO quantum dot acetone sensor is very less. The graph given below represents the transient response characteristics of ZnO quantum dots to acetone concentration of 100, 300 and 500 ppm at 300°C. By examining the graph, it can be observed that the response time and recovery time decrease with higher concentration.

At constant temperature 330°C it is observed that the acetone concentration 100ppm shows response time 94 second and recovery time 66 second, at 300ppm concentration of acetone response time observed 60 second and recovery time shifted to 51second which is less as comparison to 100 ppm concentration of acetone, at 500ppm concentration of acetone response time 50 second and corresponding recovery time 46 second

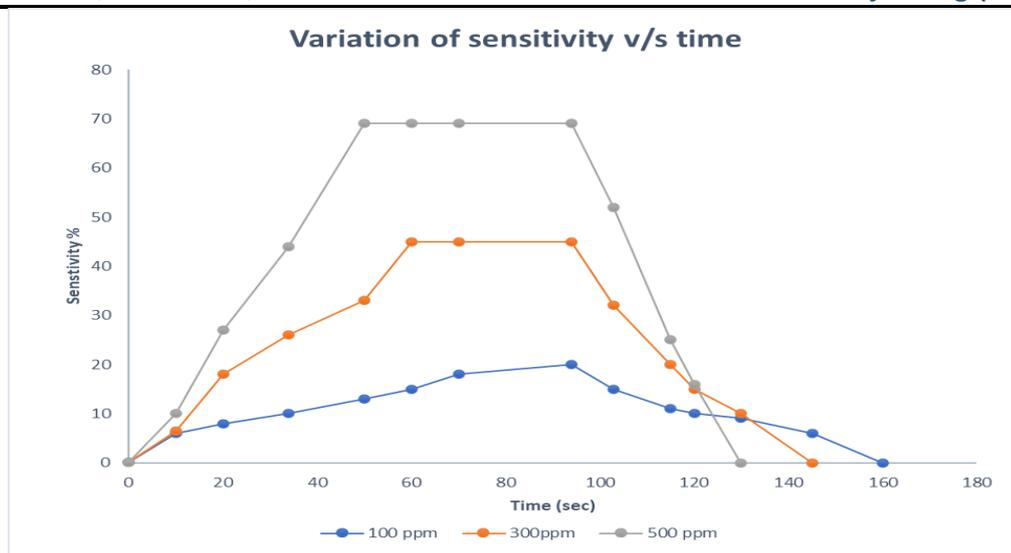


Fig 3.2: - Transient response characteristics

Recovery time for higher concentration also less than lower concentration this because at higher concentration there is excess of acetone molecule due to this there is deficiency of oxygen molecule to react with acetone molecule and form charge carrier as a result its resistivity increases immediately and its sensitivity decreases as a result recovery time reduces gaseous of higher concentration i.e., for acetone at 500ppm it is 46 second which is less than any other concentration.

3.3 Variation of Sensitivity with Operating time of Acetone Embedded in PVP matrix

The graph 3.3 given below represents the response characteristics as a function of operating temperatures for three different concentrations of 100, 300 and 500 ppm of acetone vapor. At 100 ppm, the sensitivity first increases from 10% to 25% as the temperature is raised from 230°C to 300° C and then decreases to 5 % when the temperature is further raised to 350° C. In this case the optimum operating temperature is 300° C at which the sensitivity is found to be maximum for each concentration of acetone. The quantum dots show a maximum sensitivity of 85% for 500 ppm of acetone at 300° C At relatively low operating temperature around 230°C, the response of ZnO quantum dot is restricted by slow chemical reaction (adsorption and desorption) while above 230°C, the chemical reaction occurs very fast and efficiently resulting in higher response. At 300°C response is maximum. This is attributed to the availability of sufficient adsorbed ionic species of oxygen on the ZnO surface which reacts most effectively and rapidly, with acetone molecules at this particular temperature. At higher temperatures above 300°C, the adsorbed oxygen species available at the sensing sites on the quantum dot surface are not enough to react with acetone vapor molecules. This results in a small change in resistance and hence less sensitivity. Further, it is observed that at lower concentration of acetone vapor, the sensitivity is less while at higher concentration the sensitivity is high. ZnO/ PVP sensor has better acetone sensitivity in comparison to the sensitivity of ZnO/ PVA sensor. This is due to formation of quantum dots of smaller size in a well uniformed array in the PVP matrix. By above graph 4.1 and 4.3 it can be observed that the acetone sensing property of ZnO embedded in PVA matrix at operating temperature 300°C is ranges from 21%-69 % but in ZnO/PVP sensor its sensitivity at the same temperature ranges from

62%-85% in this expect ZnO/PVP sensor is good for gas sensing but response and recovery time of ZnO/PVP sensor is more as comparison of ZnO/PVA sensor.

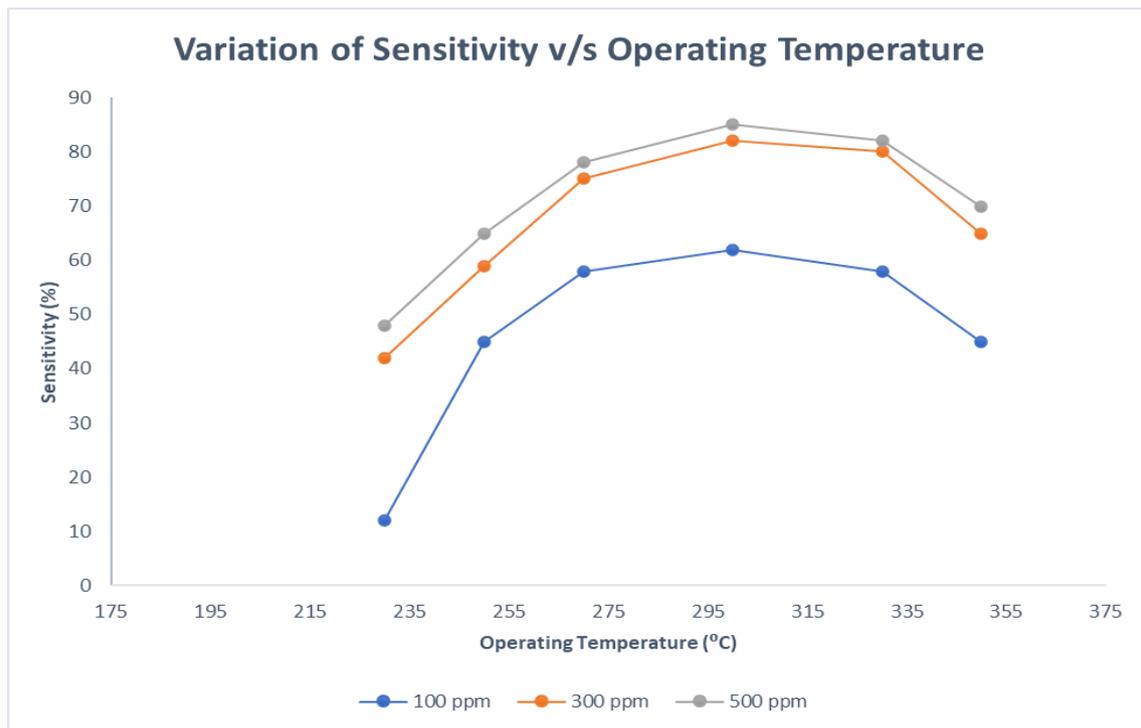


Fig-3.3 Acetone sensing with operating temperature embedded in PVP matrix

3.4 Variation of sensitivity of Ethanol with operating temperature

The graph 4.4 given below shows the response characteristics as a function of operating temperatures for three different concentrations of 100, 300 and 500 ppm of ethanol vapor. It is also observed from graph 4.4 that at lower concentration of ethanol vapor, the sensitivity is less i.e., 9% to 38%, while at higher concentration the sensitivity is higher i.e., at 300ppm and 500ppm concentration sensitivity ranges between 8.5% to 52% and 11% to 60% respectively. 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, surface reaction proceeds faster and very effectively resulting in higher sensitivity. At relatively low operating temperature around 225°C, the response of ZnO quantum dot is restricted by slow desorption as a result injected electrons are very less due to this resistivity decreases and sensitivity also decreases, while above 225°C, the desorption occurs very fast and efficiently resulting in higher response as result number of injected electrons increases and sensitivity also increases. At 296°C the response is maximum. This is attributed to the availability of sufficient adsorbed ionic species of oxygen on the ZnO surface which reacts (desorbs) most effectively and rapidly with ethanol molecule and produces large numbers of electron carriers resulting in rapid decrease in resistance and therefore its sensitivity is higher at that particular temperature.

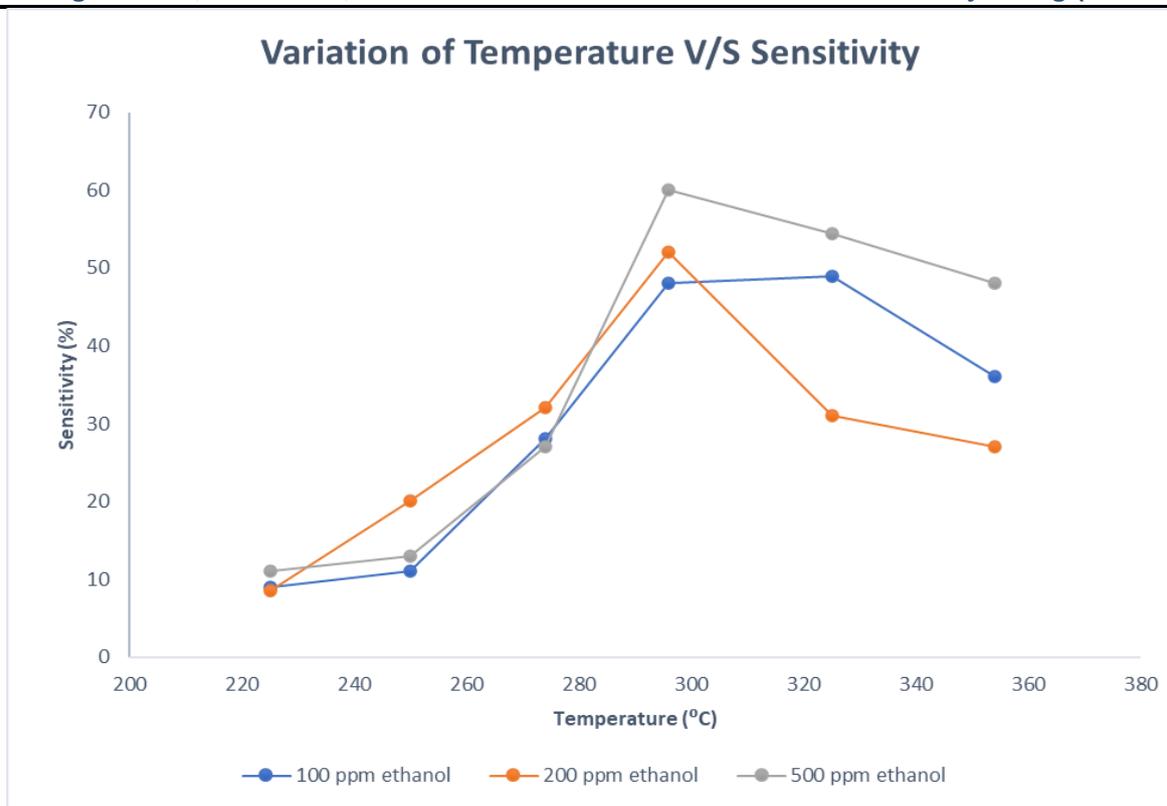


Fig 3.4 Variation of sensitivity of Ethanol with operating temperature

At temperature higher than 300°C, the amount of adsorbed (chemisorbed) oxygen is decreased with increasing temperature and change in surface coverage in chemisorbed oxygen becomes smaller and due to this reaction between oxygen species and ethanol molecule decreases and results in decrease in sensitivity.

3.5 Transient response characteristics of Ethanol

The graph given below represents the transient response characteristics of the ZnO quantum dot sensor at constant temperature 310°C of ethanol at different concentrations such as 100, 300 and 500 ppm. By graph 4.5 it can be observed that the response time decreases with higher concentration. It can be noted from the graph for 100ppm response time is 110second and corresponding recovery time is 25 second whereas at 300ppm the response time is 80 second and recovery time 15 second for concentration 500ppm response time 70 second and recovery time is 10 second. This is attributed to the fact that higher ethanol concentration favors and accelerates the desorption process resulting in faster response i.e., less response and recovery time. Its means that at higher concentration the reaction between ethanol and absorbed oxygen species occur rapidly due to this reaction between them increase as a result electron increases due to this sensitivity increases rapidly and hence response time and recovery time reduces for higher concentration of ethanol on the other hand at low concentration the reaction between adsorbed oxygen species and ethanol occur slow as comparison to higher concentration and motion of electrons become slow, as a result response and recovery time increases for lower concentration.

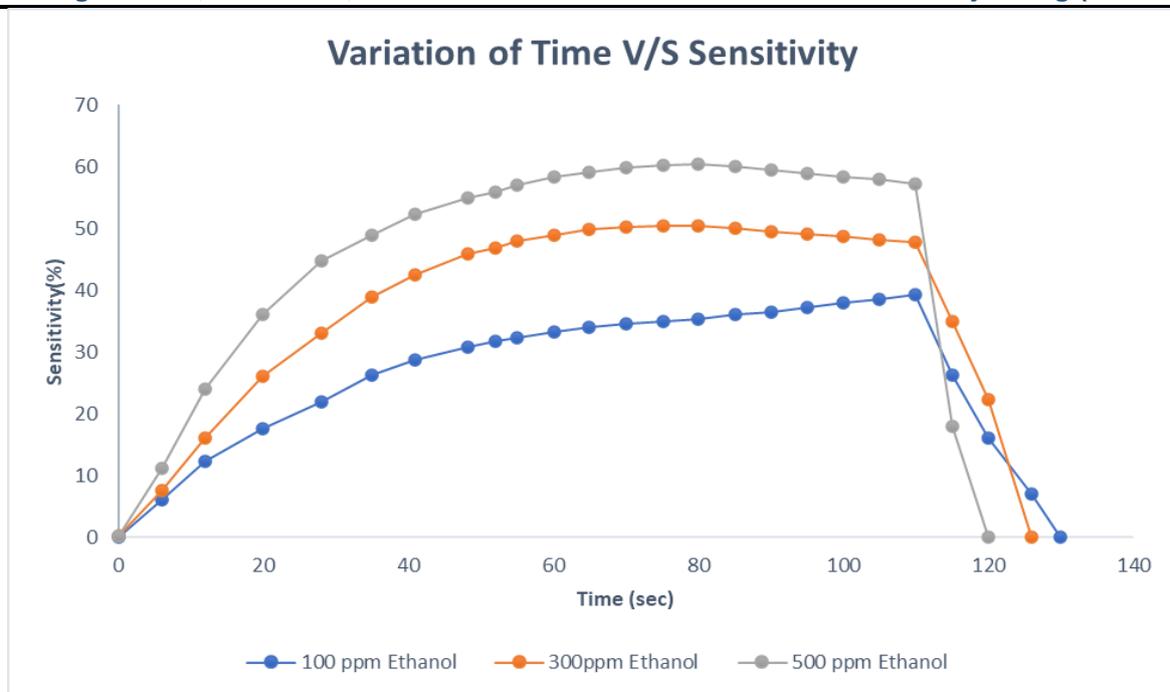


Fig 3.5: - Variation of Sensitivity v/s Time of Ethanol

3. Conclusion: -

In the present paper, Synthesis of Zinc Oxide (ZnO) Quantum Dots has been studied in detail. It is found that the ZnO/ PVP sensor has better acetone sensitivity as compared to the sensitivity of the ZnO/ PVA sensor. It observed that the response/sensitivity of ZnO quantum dots embedded on PVP matrix show maximum sensitivity of acetone vapor at 300°C which is 69%, which occurs due to saturation of redox reaction between the ethanol vapor and the adsorbed oxygen species whereas response sensitivity of ZnO Quantum Dot embedded in PVA matrix show maximum sensitivity of acetone vapor at 300°C which is 85%. This is due to formation of quantum dots of smaller size in a well uniformed array in the PVP matrix. It is also observed that ZnO/PVP quantum dot sensor responses acetone rapidly as compared to ethanol vapor but recovers ethanol more rapidly than acetone. Thus, PVP embedded ZnO quantum dots have higher acetone sensitivity.

6. References: -

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