CHAPTER 2

Literature Survey

2.1 Importance of literature survey:

Survey of literature is the first important step towards a fruitful research. The importance of literature survey can be briefly outlined into the following three points:

1. Survey of literature provides an idea about the research and development in the field opted by a researcher and forms the basis of his/her research work.

2. Survey of literature provides idea to formulate, analyze, solve a problem. It informs the researcher about the existing similar kinds of problems.

2.2. Origin of Nanoscience and Nanotechnology:

Nanoscience explores all the phenomena resulting from the transition in the nature of materials from bulk to nanoscale (1-100 nm). At nanoscale, semiconductor material behaves extraordinarily because of ‘Quantum Confinement’ or ‘Quantum Size Effect’ or ‘Size Quantization’. The nano size results in new quantum phenomena that yields some extraordinary features due to modification in bulk properties such as electrical, optical, magnetic, electronic. Thus nano materials are gateways to an enormous array of possible applications and new technologies.
2.3 Overview of recent research in the area of solid state thin film/ quantum dots gas sensor

Synthesis of semiconductor quantum dots and their different applications as various electronic and optoelectronic devices including different kinds of sensors are the frontier research areas at present\textsuperscript{[1-37]}. Recently, many techniques\textsuperscript{[14,33,34]} like molecular beam epitaxy (MBE), radio frequency sputtering (RF), liquid phase epitaxy (LPE), quenching, chemical route etc. are adopted to synthesize semiconductor quantum dots. But due to manifold advantages\textsuperscript{[14,34]} viz. like simplicity, low cost, etc. Quenching method draws the interest of recent researchers. A survey of literature has been carried out before starting our experimental work out of which a few is being illustrated below.

Al-doped zinc oxide (AZO) thin film is prepared by Mohammad et al. using spray pyrolysis technique to study their structural, optical and electrical properties \textsuperscript{[36]}. They have reported a maximum conductivity of 0.3 (Ωcm)$^{-1}$, and transmittance of 70% when prepared at substrate temperature of 430°C & 0.3% Al-doping. Maldonado et al. have fabricated Indium-doped ZnO thin films by sol-gel technique & found an average transmittance of 85% in the visible region & resistivity of $1.3\times10^{-2}$ Ωcm \textsuperscript{[1]}. Nanto et al. have prepared ZnO thin film for ammonia gas detection and obtained high sensitivity & excellent selectivity \textsuperscript{[3]}. Chemically deposited ZnO thin films have been prepared by Mitra et al. to sense the presence of reducing gases, e.g. H$_2$ & LPG in ambient atmosphere \textsuperscript{[4]}. They have reported a high sensitivity (more than 99%) for 3 vol% hydrogen and 88% sensitivity for 1.6 vol% LPG in air & they also found that Pd sensitization lowers the film conductance & improves the sensitivity significantly.
ZnO thin films have been prepared by Shinde et al. using chemical spray method & they studied the effect of molarity of precursor solution on the LPG sensing characteristics\[5\]. They have reported the shortest response & recovery time of 84 & 90 sec respectively compared to Mitra et al. Mehra et al. have studied the changes of structural, optical and electrical properties of sol-gel derived ZnO films with their thickness\[6\].

Misra et al. has prepared the tin oxide thin film by sol-gel technique to study the alcohol sensing properties of the film and found that the films are sensitive at very low concentration (100 ppm) of alcohol\[7\]. Egashira et al. have reported the effect of gas diffusivity and reactivity on sensing properties of thick film SnO2 based sensors\[8\]. Fallah et al. have fabricated tin-doped indium oxide films on glass substrate at low temperature and studied the effect of deposition rate on the electrical, optical, and structural properties of the film\[9\].

Patel et al. have carried out a remarkable work by synthesizing Indium tin oxide (ITO) thin film for detection of methanol at room temperature\[10\]. A significant improvement of sensitivity, selectivity, lower detection limit, and stability in the film has been observed in their work by depositing ITO films over ultra thin Cu stimulator film. This approach is promising towards improvement in the performance of gas sensors at room temperature. Makhija et al. have prepared Indium oxide thin film for the detection of ammonia gas and ethanol vapor and found that the sensitivity is independent of the thickness of the film for ethanol vapors while it is dependent on thickness for ammonia gas\[11\]. It is reported by Shriram et al. that acetone sensitivity in semiconductor microstructures increases with higher doping concentration of impurity like cobalt\[35\]. Further, Sahay has
reported acetone sensing by ZnO thin film but it is of long response and recovery time \textsuperscript{12}. Nath et al. have reported the synthesis of ZnS and ZnS:Cu (copper doped ZnS) quantum dots by chemical method at room temperature \textsuperscript{13}. In this technique ZnS and ZnS:Cu quantum dots are produced by simple chemical reactions where zeolite acts as matrix and plays the key role in controlling particle growth during synthesis. ZnS exhibits luminescence properties such as Zn\textsuperscript{2+} related emission. ZnS:Cu possesses Cu related emission, efficient low voltage electroluminescence, and super linear voltage-brightness electroluminescence characteristics. This study demonstrates the technological importance of semiconductor quantum dots prepared by low cost chemical route.

Mohanta et al. have reported the synthesis and optical absorption study of energetic ion-irradiated hydroxyl-free ZnO semiconductor quantum dots. Quantum dots samples are synthesized by a quenching technique and 100-MeV chlorine ion is selected for the irradiation experiment with doses 1\times10^{11}, 5\times10^{12} ions/cm\textsuperscript{2} \textsuperscript{14}. They have observed the optical absorption spectra of irradiated quantum dots reveal that red shift of the energy-gap parameter with respect to unirradiated (virgin) quantum dots. The narrowing of the energy gap of nanoparticles indicate particle growth under ion irradiation which is confirmed from transmission electron microscope images. The possible reason for such variations is encountered using an effective-mass approximation model.

Al-doped ZnO thin film are prepared by Sahay et al. using spray pyrolysis technique to study the sensing properties of the films towards methanol vapor \textsuperscript{15}. They have reported that sensitivity is found to be maximum at around 275\textdegree C in all the films.
Further the films shows fast response & recovery to methanol vapor at higher operating temperature.

Joseph et al. have prepared Aluminium-doped zinc oxide films by chemical spray pyrolysis technique [16]. Variation of structural, morphological, electrical and optical properties with doping concentration was investigated in detail. It was observed in their study that the films are highly transparent to visible radiation and electrically conductive. XRD studies have shown that the films are polycrystalline in nature with (0 0 2) preferred orientation. SEM studies have revealed the smooth polycrystalline morphology of the films. It was found that the films deposited at optimum conditions exhibited a resistivity of $2.45 \times 10^{-4}$ Ωm with an optical transmittance of 97% at 550 nm.

Fang et al. have fabricated SnO$_2$ thin film ethanol gas sensor by electron-gun evaporation and proper annealing in ambient oxygen gas [17]. It has been revealed that the prepared sensor has high sensitivity and selectivity in detecting ethanol gas.

Peng et al. have synthesized Copper-doped zinc oxide (ZnO) (1 mol%) nanocrystals using a sol–gel method and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), inductive coupled plasma with optical emission spectrometry (ICP-OES) [18]. The XRD result indicates that the introduction of copper has no influence on the crystal structure of ZnO, though ICP-OES exhibits the molar ratio of copper and zinc was 0.86:100. The gas response of the copper-doped ZnO is also studied to ethanol and acetone without and with the illumination of 355 nm light. It is found that the ultraviolet light irradiation could enhance the gas response, and the mechanism with irradiation is discussed. Their results demonstrate
that light irradiation is a promising approach to achieve large response at room temperature.

Chakraborty et al. have studied the thiourea treatment on the recovery time of tin-dioxide based sensor for detection of methane. Though the response time remains almost the same \[^{19}\], the thiourea treatment improves the long term stability of the sensors.

Nath et al. have prepared thin film tin dioxide (SnO\(_2\)) by spray pyrolysis method to study the sensing characteristics of the prepared film at various temperatures & concentration level of ethanol \[^{20}\].

Achour et al. have prepared Al-doped ZnO semiconductor thin films by spray pyrolysis to study their optical, electrical and structural properties \[^{37}\].

Vaishnav et al. have prepared Indium Tin Oxide (ITO: In\(_2\)O\(_3\) + 17% SnO\(_2\)) thin films grown on alumina substrate at 648 K temperatures using direct evaporation method with two gold pads deposited on the top for electrical contacts are exposed to ethanol vapours (200–2500 ppm) \[^{21}\]. The operating temperature of the sensor is optimized. The sensitivity variation of films having different thickness is studied. The sensitivity of the films deposited on Si substrates is studied. The response of the film with MgO catalytic layer on sensitivity and selectivity is also observed. A novel approach of depositing thin stimulating layer of various metals/oxides below the ITO film is tried and tested.

Hulser et al. have reported that SnO\(_2\) nanoparticles with small particle size distribution (\(\sigma < 1.2\)), and diameters of 10, 15 and 20 nm are deposited on platinum interdigital transducers with 2 m finger width and 2 m spacing. Impedance
spectroscopy measurements in synthetic air, taken in the temperature range between 100 and 250°C show a clear dependence of the measured impedance on the particle size. Three different contributions to the overall impedance have been resolved for 10 nm particles and assigned to the contribution of bulk, inter-granular contact and electrode contact. Particles of larger diameters do not allow such a clear distinction. The experimental observations have been analyzed by fitting the measured data with equivalent circuit functions, where typical serial connections of simple R(resistance) and parallel RCs(resistance & capacitance) are used for fitting. As expected for a semiconducting material, the resistance decreases with increasing temperature. Activation energies of the different charge carrier transport processes are determined[22].

Chou et al. have prepared the ZnO:Al thin films by RF(radio frequency) magnetron sputtering on Si substrate using Pt as inter digitated electrodes [23]. The structure is characterized by XRD and SEM analyses, and the ethanol vapor gas sensing as well as electrical properties have been investigated and discussed. The gas sensing results show that the sensitivity for detecting 400 ppm ethanol vapor was ~20 at an operating temperature of 250°C. The high sensitivity, fast recovery, and reliability suggest that ZnO:Al thin film prepared by RF magnetron sputtering can be used for ethanol vapor gas sensing.

Shouli et al. have investigated Novel CH₄ gas sensors made of the nanocomposites of Sn/In/Ti oxides. The nano sized crystalline oxides and their composites are successfully prepared by a sol–gel and controlled precipitation method, respectively, through manipulating the salts concentration, precipitation pH value, aging time and composition of composites [24]. The derived precursors exhibit superior thermal
stability. To ensure sufficient crystallinity and insignificant grain growth of the materials, the appropriate calcinations temperatures are 600°C for 4 h(hour) and 700°C for 2 h for the precursors of oxides and composites, respectively. The performance and structure of the composites were characterized by EDX, TEM, BET, TG–DTA and XRD. The sensing tests show that these nano composites exhibited high response and selectivity for the detection of CH$_4$ at operating temperatures between 200°C and 250°C and the response depends on the composition of composites, calcinations temperature, operating temperature and gas concentration in air. The gas sensing mechanism of the sensors is also discussed by X-ray photoelectron spectroscopic (XPS) and temperature-programmed desorption (TPD) studies.

Rao has investigated Sensitivity characteristics of ZnO-based semi-conductor gas sensors to ethanol vapors with lanthanum oxide and palladium $^{[25]}$. The sensitivity of the sintered elements are promoted by the addition of La$_2$O$_3$ and Pd. Further, the sensor operating temperature is reduced with the noble metal. These elements have been tested for cross sensitivity for different gases and it has been confirmed that these are highly sensitive and selective for ethanol vapors at 175°C in air atmosphere. The promoting effect of the sensitivity of the sensor elements with lanthanum oxide seems to be related to the selectivity to oxidation of ethanol vapors.

Sahay et al. have studied the electrical characteristics of ZnO thin films prepared by spray pyrolysis, for ethanol sensors $^{[2]}$. The sensitivities of the films are measured at various temperatures and concentrations of ethanol. It is observed that the sensitivity increases with increasing working temperature. At higher ethanol concentrations, the sensitivity increases more rapidly with increasing temperature.
Further, the films showed fast response and recovery times at higher working temperatures. The sensing mechanism of the films towards ethanol vapor has been explained.

Prajapati et al. have reported that ZnO nano-particle thin films are deposited on cleaned glass substrates by spray pyrolysis technique using the precursor solution of zinc acetate dihydrate \([\text{Zn(\text{CH}_3\text{COO})_2\cdot2\text{H}_2\text{O}}]\) \(^{[26]}\). Structural analyses and surface morphology of the resulting films are carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD analyses confirm that the films are polycrystalline zinc oxide, possessing hexagonal wurtzite structure with crystallite size ~25 nm. The SEM micrograph of the film shows a good uniformity and a dense surface having spherical-shaped grains. Alcohol sensing characteristics deposited films has been investigated for various concentrations of methanol, ethanol and propan-2-ol in air at different operating temperatures. At 150 ppm concentration, the film shows maximum response (85.2%) to propan-2-ol at the operating temperature of 250°C; whereas at the same concentration 150 ppm, the maximum responses to methanol and ethanol at 300°C are observed to be 75.8% and 52.4%, respectively. Also, the film exhibits selective high response to propan-2-ol, followed by ethanol and methanol, respectively at each operating temperature up to 275°C. This selectivity is more pronounced in the region of lower operating temperatures and concentrations.

Mitra et al. study the liquid petroleum gas (LPG) sensitivity characteristics of zinc oxide (ZnO) films for an optimized level of Pd loading \(^{[4]}\). The sensor element comprises of a layer of chemically deposited ZnO on which an overlayer of palladium (Pd) sensitiser is formed by a chemical dipping technique. The room
temperature resistance of the film is found to be a sensitive function of the quantity of palladium loading, which can be optimized for stable and reproducible sensor properties. The sensor characteristics that are dependent also on the operating temperature can be optimized at around 250°C. A sensitivity of 88% is observed in presence of 1.6 vol.% LPG in air at this optimum temperature with reasonably fast response and recovery times.

Shishiyanu et al. fabricate NO₂ gas sensor by successive ionic layer adsorption and reaction (SILAR) technique and rapid photothermal processing (RPP) of the Sn-doped ZnO film [27]. McAleer et al. describe a novel type of gas sensor, which relies on the thermo voltage generated when one region of a porous semiconductor is heated by the reaction of a combustible gas with oxygen [28]. One of the main attractions of this type of sensor is that the power requirements are minimal. Use is made of a voltage measurement, which distinguishes the device from other semiconductor gas detectors that depend upon the measurement of resistance.

Mitra et al describe the electrical and gas sensing properties of chemically deposited zinc oxide (ZnO) films [29]. Two activation energy values, 0.3 eV and 0.8–0.9 eV, are determined in the temperature range 300–400 K which are attributed to oxygen vacancy (V₀) donor and heat of chemisorption of the O₂⁻ species. The adsorption of oxygen on ZnO leads to a stable and highly resistive surface suitable for sensor operation in the resistive-mode. A high sensitivity (S>99%) is observed for 3 vol% hydrogen (H₂) in air along with a strong surface reduction. For liquid petroleum gas (LPG), a high sensitivity (S=50–75%) is observed in the 0.4–1.6 vol% concentration range in air which is an important commercial range for LPG alarm development.
Muthuraja et al. report that gas monitoring devices consisting of metal oxide thin films have been very widely applied as chemical sensors \cite{30}. They find profound use towards detection of toxic pollutant gases and organic vapors. They provide beneficiary merits as large scale commercial sensors owing to their low price, small size, high sensitivity and consume very low power. Ethanol is one of the most commonly and extensively used alcohol, both in the fields of research and industrial applications. There is an imminent need to develop sensors for its detection with very sensitivity. In this study, Zinc oxide nanoparticles are prepared by a suitable soft chemical method. ZnO thick films are prepared from these nanoparticles by dip coating method. ZnO thick films are coated on an Alumina substrate and the sensor is tested for ethanol for 50 ppm at various temperatures. The sensor is found to operate with maximum efficiency at an optimum temperature of 350°.

Roy and Basu have reported that Zinc oxide (ZnO) is a versatile material for different commercial applications such as transparent electrodes, piezoelectric devices, varistors, SAW devices etc because of its high piezoelectric coupling, greater stability of its hexagonal phase and its pyroelectric property \cite{31}. In fact, ZnO is a potential material for gas sensor applications. Good quality ZnO films are deposited on glass and quartz substrates by a novel CVD technique using zinc acetate as the starting solution. X-ray diffraction confirmed the crystallinity of the zinc oxide film and SEM study reveals uniform deposition of fine grains. Undoped ZnO films are used for detection of dimethylamine (DMA) and H2 at different temperatures by recording the change in resistivity of the film in presence of the test gases. The response is faster and the sensitivity is higher compared to the earlier
reported ZnO based sensors. The operating temperature is found to play a key role in the selectivity of such sensors.

Tan et al. have reported that the optical band gap of ZnO thin films deposited on fused quartz by metal-organic chemical-vapor deposition is studied [32]. The optical band gap of as-grown ZnO blue shifted from 3.13 to 4.06 eV as the growth temperature decreased from 500 to 200°C. After annealing, the optical band gap shifted back to the single-crystal value. All the ZnO thin films studied show strong band-edge photoluminescence. X-ray diffraction measurements show that samples deposited at low temperatures (<450°C) consist of amorphous and crystalline phases. The red shift of the optical band gap back to the original position after annealing is strong evidence that the blue shift is due to an amorphous phase. The unshifted photoluminescence spectra indicates that the luminescence is due to the crystalline phase of ZnO, which is in the form of nanocrystals embedded in the amorphous phase.

Based on this literature survey, the present study is carried out.
References:


