



“STUDY OF PROPERTIES AND CHARACTERIZATION OF MNPs of ZnO FOR GAS SENSOR APPLICATIONS”

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Abstract

MNPs of ZnO have great potential applications in the fields of optoelectronic and sensor devices. Therefore, it is very important to realize the controllable growth of MNPs of ZnO and investigate their properties. ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications. ZnO is a versatile functional material that has a diverse group of growth morphologies. MNPs of ZnO are easily formed even on cheap substrates such as glass and hence they have a promising potential in the nanotechnology future. The present work involves the study of MNPs of ZnO by chemical precipitation method, studying growth, microstructure, and morphology and from that correlating the microstructure to its properties. At the beginning, efforts have been made to optimize the deposition conditions. It is needless to mention that the properties of the MNPs depend extensively on the growth conditions, which influences its microstructure. Different parameters like substrate temperature, PH of solution, deposition time, annealing etc. were carefully monitored to decide the optimized growth condition of the MNPs.

MNPs of ZnO are also attractive for sensor and biomedical application due to its bio-safety and large surface area. The next objective of this study is to detect the gas sensing for MNPs of zinc oxide for different applications.

1. Introduction

As an important future technology, nanotechnology presents an opportunity for positively influencing economic development in the long term through intensive research and the effective translation of the research results into innovative products. Nanotechnology describes the production, investigation and application of structures, molecular materials and inner boundary surfaces having at least one critical dimension below 100 nm. The low end of the nanometer range borders on the molecule size range which has long been shaped by targeted chemical reactions. The upper nanometer range encompasses microtechnology which is also undergoing a dynamic development through, for example, computer technology (integrated circuits). [1] During the last decade, scientists have developed techniques for synthesizing and characterizing many new materials with at least one dimension on the nanoscale, including nanoparticles, nanolayers, and nanotubes. [2] Still, the design and synthesis (or fabrication) of nanoscale materials with controlled properties is a significant and ongoing challenge within nanoscience and nanotechnology. Recently, a few semiconductor nanocrystals, such as CdS and ZnS, have been developed for fluorescent labeling, a potentially useful biomedical application. [3,4] Although they exhibit much greater photostability than commercial organic dyes, they have two significant problems when directly applied *in vivo*. First, semiconductor nanocrystals containing metal ions such as cadmium or selenide are, unless contained, toxic to human health. In spite of its importance, there are few studies regarding their toxicities or safety in living organisms.[5] Second, since most highly luminescent semiconductor nanocrystals are grown in hydrophobic media, they are incompatible with mainly hydrophilic biological systems. To overcome this, their surface properties, or indeed the semiconductor nanocrystals themselves, should be modified. In this regard, there are several reports on solubilized hydrophobic nanocrystals in water [6-8]. ZnO is an important semiconductor owing to its unique electronic and optical properties, and its potential applications in solar energy conversion, nonlinear optical, photoelectrochemical cells and heterogeneous photocatalysis [9-10]. Nowadays, the products of semiconductor industry spread all over the world and deeply penetrate into the daily life of human being. The starting point of semiconductor industry was the invention of the first

semiconductor transistor at Bell Lab in 1947. Since then, the semiconductor industry has kept growing enormously. In the 1970's, the information age of human being was started on the basis of the stepwise appearance of quartz optical fiber, III-V compound semiconductors and gallium arsenide (GaAs) lasers. During the development of the information age, silicon (Si) keeps the dominant place on the commercial market, which is used to fabricate the discrete devices and integrated circuits for computing, data storage and communication. Since Si has an indirect band gap which is not suitable for optoelectronic devices such as light emitting diodes (LED) and laser diodes, GaAs with direct band gap stands out and fills the blank for this application. As the development of information technologies, the requirement of ultraviolet (UV)/blue light emitter applications became stronger and stronger which is beyond the limits of GaAs. Therefore, the wide bandgap semiconductors such as SiC, GaN and ZnO, i.e. the third generation semiconductors, come forth and turn into the research focus in the field of semiconductor. ZnO is a typical II-VI semiconductor material with a wide bandgap of 3.37 eV at room temperature. Although its bandgap value is closer to GaN (3.44 eV), its exciton binding energy is as high as 60 meV, which is much larger than that of GaN (21 meV) and even room temperature thermal excited energy (25 meV). Therefore, theoretically, we can harvest high efficient UV exciton emission and laser at room temperature, which will strongly prompt the applications of UV laser in the fields of benthall detection, communication and optical memory with magnitude enhancement in the performance. Moreover, the melting point of ZnO is 1975 oC, which determines its high thermal and chemical stability. Plus, ZnO has owned a huge potentially commercial value due to its cheaper price, abundant resources in the nature, environment friendly, simply fabrication process and so on. Therefore, ZnO has turned into a new hot focus in the field of short-wavelength laser and optoelectronic devices in succession to GaN in the past decade. In fact, the research interest in ZnO has waxed and waned over the years. The first enthusiasm started studies of the lattice parameter by M.L. Fuller in 1929 [11] and C.W.Bunn in 1935[12], but the enthusiasm flagged with the difficulty in producing p-type doping and high quality crystal crystalline material. Until 1997, Tang at al reported, for the first time, the room-temperature ultraviolet (UV) laser emission from self-assembled ZnO microcrystallite thin films [13-14]. Zinc oxide is an inorganic compound with the formula ZnO. ZnO is a white powder that is insoluble in water, which is widely used as an additive in numerous materials and products including plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, and first aid tapes. It occurs naturally as the mineral zincite but most zinc oxide is produced synthetically. In materials

science, ZnO is a wide-bandgap semiconductor of the II-VI semiconductor group (since oxygen was classed as an element of VIA group (the 6th main group, now referred to as 16th) of the periodic table and zinc, a transition metal, as a member of the IIB (2nd B), now 12th, group). The native doping of the semiconductor (due to oxygen vacancies) is n-type. This semiconductor has several favorable properties, including good transparency, high electron mobility, wide bandgap, and strong room-temperature luminescence. Those properties are used in emerging applications for transparent electrodes in liquid crystal displays, in energy-saving or heat-protecting windows, and in electronics as thin-film transistors and light-emitting diodes. Zinc oxide is an important n-type semiconductor with a direct band gap of 3.37 eV. Zinc oxide nanoparticles are widely used in various applications such as optical devices, catalysis, light emitting diodes, photo detectors, solar cells and gas sensors. Zinc is an essential nutrient in humans and animals for many physiological functions, including immune and antioxidant function, growth, Skeleton development, skin growth, appetite, wound healing and reproduction. Zinc oxide (ZnO), a safe source for Zn supplementation and it is commonly used to fortify foodstuff in the food industry. ZnO will decompose into Zn ions after consumption. A variety of methods have been used for the synthesis of zinc oxide nanoparticles such as direct precipitation, homogeneous precipitation, solvothermal method, sonochemical method, reverse micelles, sol gel method, hydrothermal, thermal decomposition, and microwave irradiation.

Properties of Zinc Oxide

In addition to cost savings, ZnO offers the following properties.

- High carrier mobility
- Transparency
- Wide band gap
- Low temperature process

The high carrier mobility is directly linked to transparency, which makes it fully possible for ZnO to compete with existing silicon materials. The wide band gap is important because it opens the possibility of creating Ultra Violet (UV) LEDs and white LEDs with superior color purity. Low temperature processing is preferred in some applications such as OLEDs. ZnO has a direct band gap energy of 3.37 eV at room temperature, and exciton and biexciton energies of 60 meV and 15 meV,

respectively. Epitaxy will likely further improve ZnO exciton properties, which directly relates to the optical properties in photovoltaics and displays.

Zinc oxides as transparent semiconductors are attracting interest mainly because there has been a sharp jump in the need for higher carrier mobility of transparent semiconductors. The carrier mobility determines transparent TFT characteristics. This is now exceeding the carrier mobility of materials such as low-temperature poly-Si (LTPS) and amorphous Si used in LCD panels.

2. Review of Literature

Nanoscience is still largely in the "discovery phase" where in new materials are being synthesized (using any means available) on small scales (100s of milligrams or less) for testing specific physical properties. Typically, during this phase of development of a new technology area, researchers focus mainly on identifying new properties and applications. Nanoparticles and other nanomaterials that exhibit size-dependent properties are already finding application in products ranging from consumer healthcare goods to high performance composites [20]. In addition, a growing number of applications of nanoscience/nanotechnology are being developed that promise environmental benefit including new catalysts for environmental remediation,[21] cheap and efficient photovoltaics, [22] thermoelectric materials for cooling without refrigerants, [23] lightweight (and thus energy-conserving) nano composite materials for vehicles,[24] miniaturized devices that reduce material consumption, and sensors that eliminate the need for (often) wasteful wet chemical analyses. Nanoscale sensors [25] can also offer faster response times and lower detection limits, making on-site, real-time detection possible. Nano Meter scale of Particle size of material is aim of Nanotechnology development that is taking place to produce smaller, faster, lighter and cheaper devices with greater and multi functionality while using less raw materials and consuming less energy. Nanotechnology is concerned with materials and systems where structure and component exhibit novel and significantly improved physical, chemical and biological properties, phenomenon and processes because of their minaturization of size i.e. nano-scale size structural features in the range of 10^{-9} to 10^{-7} m (1 to 100nm). More generally nanotechnology can be defined as any technique able to work at submicron scale. Research on nanomaterials is a step towards the minaturization of technology that will contribution significantly towards a sustainable usage of raw material and energy. It is an interdisciplinary science involving physics, chemistry, biology, engineering material science, computer science etc [26-28]. On Dec. 29, 1959, at the California

Institute of Technology Nobel Laureate Richard P. Feynman gave a talk at the annual meeting of the American Physical Society that has become one of the twentieth century's classic science lectures, titled "There's Plenty of Room at the Bottom"[29]. He presented a technological vision of extreme miniaturization several years before the word "chip" became part of the lexicon. He talked about the problem of manipulating and controlling things on a small scale. Extrapolating from known physical laws, Feynman envisioned a technology using the ultimate toolbox of nature, building nano objects atom by atom or molecule by molecule. Since the 1980s, many inventions and discoveries in the fabrication of nano objects have become a testament to his vision. In recognition of this reality, the National Science and Technology Council (NSTC) of the White House created the Interagency Working Group on Nanoscience, Engineering and Technology (IWGN) in 1998. In a January 2000 speech at the same institute, former President William J. Clinton talked about the exciting promise of nanotechnology and, more generally, the importance of expanding research in nanoscale science and technology. Later that month, he announced in his State of the Union Address an ambitious \$ 497 million federal, multi-agency National Nanotechnology Initiative (NNI) in the fiscal year 2001 budget, and made it a top science and technology priority [30, 31]. The objective of this initiative was to form a broad-based coalition in which academe, the private sector, and local, state, and federal governments would work together to push the envelope of nanoscience and nanoengineering to reap nanotechnology's potential social and economic benefits. Nanotechnology literally means any technology performed on a nanoscale that has applications in the real world. Nanotechnology encompasses the production and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology is likely to have a profound impact on our economy and society in the early twenty-first century, comparable to that of semiconductor technology, information technology, or cellular and molecular biology. Science and technology research in nanotechnology promises breakthroughs in such areas as materials and manufacturing, nanoelectronics, medicine and healthcare, energy, biotechnology, information technology, and national security. It is widely felt that nanotechnology will be the next industrial revolution.

Although several applications of nanotechnology already exist in our daily life, we believe that the vast majority of new innovative products and applications enabled by nanotechnology are still hidden in the future. Examples of currently deployed nanotechnology products are: Nanoelectronics, Processor chips, high density memory, CCD chips (Moore's law), Opto-electronics MEMS devices such as ink-jet print heads, Pressure and flow sensors, Inertial motion units DNA biochips,

Membranes, Fuel cell components Nanosized pigments and additives (UV-blockers) in paints, Coatings, Lubricants and Cosmetics Nanoclay reinforced materials With the growing number of nanotech research groups and growing worldwide R&D budget, the number of nanotechnology developments has increased enormously with a subsequent growth and broadening of the potential nanotech product portfolio [32]. Future nanotechnology products are expected to arise in the areas: RFID-tags with Nanosensors: Sensor tags, μ -power, Distributed, Wireless, autonomous sensors, Adaptive materials with built-in sensors and actuators, Nanobio, Nanowire and Biotransistors, Nanomedicine

The area is so large now that sub-areas have been formed such as Nanoelectronics, nanomedicine, nanobio, nanomaterials, nanofibers, nanosensors, nanomachines, nanobots and many more. Some examples of these sub-areas are reviewed in the appendix. By fusing nanotechnology with other technologies such as bio, the R&D nanoworld is expanding rapidly in many directions.

We are study few papers related with Nanoparticles i.e.II-VI semiconductors such as Zones, CdS, ZnO, CdTe are the foremost promising materials and much in demand for optical and optoelectronic applications [33-35]. Among these semiconductors Zones has wide band-gap energy of 3.68 eV for bulk cubic phase and 3.80 eV for bulk hexagonal phase [36]. Due to large band gap, ZnS is an essential phosphor host lattice material for electroluminescent devices. It is one of the most important materials in photonics owing to its high transmittance in visible region and high index of refraction (about 2.2) [37]. It has been used as a reference material to test several theoretical models in condensed matter physics [38]. ZnS nanoparticles capped with cetyltrimethylammonium bromide, thioglycerol, ethylene glycol, methacrylic acid, polyvinyl pyrrolidone have been prepared, respectively, using microemulsion, hydrothermal, solvolthermal/hydrothermal, sol-gel, chemical vapor deposition [39-43]. These nanoparticles are much sought-after for applications in CRT screens, catalysts, optical waveguides, reflectors, anti-reflecting films, etc. [44- 47]. Different types of dopants with different concentrations have been used to enhance the optical properties of ZnS nanoparticles. These nanoparticles doped with optically active centers have been found useful in fluorescent bio-labeling [48] whereas, those doped with transition metal ions or rare earth ions used as phosphors [49] [42]. Investigations have also been made on the photophysical and photochemical properties of ZnS nanomaterials doped with Cu, Co, Eu, Ce, Mn, Ag and Er [50-52]. Keeping the above points in view, considerable experimental work has been performed in the past in order to synthesize and understand the properties of ZnS nanoparticles with/without capping agent and dopant, for various applications. One of the applications of ZnS is in reflective coatings. A reflective

coating is an engineered formulation of pigment, binder, solvent and additives that mix to create a specific product with its own reflective characteristics [53].

Semiconductor nanoparticles doped with transition metal ions have attracted wide attention due to their excellent luminescent properties [54-56]. The doping of transition metal ion such as Mn, Cu, Co etc opens up possibilities of forming new class of material and new properties of the material are expected. The transition metal doped nanoparticles show different optical properties corresponding to their host counterparts. These nanoparticles have found tremendous application in optical light emitting diodes [57-60]. In undoped II-VI semiconductors such as CdS, CdTe, CdSe and ZnS, the band gap is engineered by controlling the crystal size, leading to a tunable band edge emission. By doping the nanoparticles with luminescent activators, the excitation can be tuned by quantum size effect while the activator related emission is largely unchanged. Various efforts have been made by the researchers to dope transition metal ions in nanomaterials. P.H. Borse et al [61] have reported the luminescence quenching in ZnS nanoparticles due to Fe and Ni doping. They found that the blue light emission in ZnS nanoparticles could be completely quenched when doped with iron and nickel. M. Marandi et al [62] have studied the thermo-mechanical growth of Mn doped CdS nanoparticles and found that a prolonged reaction time decreases the intensity of Mn luminescence peak to about 35% of the original value. Doped nanostructured II-VI semiconductors have been used extensively due to their industrial implementation in nanoelectronic devices [63-64]. It would be interesting to study the electrical properties of pellets of transition metal doped nano-particles of semiconductors and the effect on the electrical properties due to increase in temperature for its implementation in the device fabrication.

Nanotechnology can provide high durability for fabrics, because Nano-particles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics and leading to an increase in durability of the function. In addition, coating of nano-particles on fabrics will not affect their breathability or hand feel. It is concerned with materials whose structures exhibit significantly novel and improved physical, chemical, and biological properties and functionality due to their nanoscaled size (Ratner and Ratner, 2002). The intrinsic properties of metal nanoparticles are mainly determined by size, shape, composition, crystallinity and morphology. Nano finishing is concerned with positive control and processing technologies in the sub nano meter range (Russell, 2002). Coating is a common technique used to apply nano-particles onto textiles. The coating compositions that can modify the surface of textiles are usually composed of nano-particles, a surfactant, ingredients and a carrier medium Several methods can apply coating onto fabrics,

including spraying, transfer printing, washing, rinsing and padding. Of these methods, padding is the most commonly used.

Comfort and protection are two very important aspects of textiles today. Basically, with a view to protect the wearer and the textile substrate itself, antimicrobial finish is applied to textile materials. Antibacterial protection (additives) inhibits the growth of such bacteria and allergens. Today many research groups in physics, chemistry or biology are working on fabricating multicomposite films by LBL assembly that may lead to prototypes of devices like in optics, bio-sensing, separation membranes, technical textile (Hinestroza, Hyde and Rusa, 2005) and antimicrobial property. Polymer thin film can be deposited directly onto textile fabrics by following Layer-by-Layer (LBL) deposition technique to produce Polyelectrolyte Multilayers (PEM). The PEM method has opened the way for the easy preparation of truly nano-composite textiles containing a wide range of molecules and nanoparticles allowing the preparation of new technical fibers.

Gas sensor devices have traditionally comprised thin films of metal oxides, with tin oxide, zinc oxide and indium oxide being some of the most common materials employed. With the recent discovery of novel metal oxide nanostructures, sensors comprising nanoarrays or single nanostructures have shown improved performance over the thin films. The improved response of the nanostructures to different gases has been primarily attributed to the highly single crystalline surfaces as well as large surface area of the nanostructures.

Zinc Oxide Films for Gas Sensing Applications

Using zinc naphthenate dissolved in xylene as a precursor undoped ZnO nanopowders were synthesized by the flame spray pyrolysis technique. The average diameter and length of ZnO spherical and hexagonal particles were in the range of 5 to 20 nm, while ZnO nanorods were found to be 5–20 nm wide and 20–40 nm long, under 5/5 (precursor/oxygen) flame conditions. The gas sensitivity of the undoped ZnO nanopowders towards 50 ppm of NO₂, C₂H₅OH and SO₂ were found to be 33, 7 and 3, respectively. The sensors showed a great selectivity towards NO₂ at high working temperature (at 300 °C), while small resistance variations were observed for C₂H₅OH and SO₂, respectively.

Zinc oxide has attracted increased attention during the last few years due to the possibility of its relatively simple transformation into various nanoscale structures. Nanostructures like rods and

particles have become the most promising research materials because of their wide range of applications. Different techniques, namely sol-gel, spray pyrolysis, hydrothermal method, electrospinning, thermal evaporation, *etc.* are prevalent for the synthesis of zinc oxide nanoparticles and nanorods. In the present work, nanorods and nanoparticles have been prepared by flame spray pyrolysis (FSP), a promising technique for the synthesis of high purity nano-sized materials with controlled size and crystallinity in a single step. This was systematically investigated by using an external-mixing gas-assisted atomizer supported by six premixed methane-oxygen flamelets.

Semiconducting metal oxide sensors have been extensively studied due to their simple preparation and high sensitivity under ambient conditions. Zinc oxide (ZnO), an n-type metal oxide semiconductor sensing material with a wide band gap ($E_g = 3.37$ eV at 300 K), has attracted much attention due to its high chemical stability, low cost, and good flexibility in fabrication. It was found that ZnO exhibits pronounced gas sensing properties towards many toxic/non-toxic gases such as NO₂, SO₂, ethanol, *etc.* A summary on the sensing properties toward NO₂, ethanol (C₂H₅OH) and SO₂ gases of the undoped ZnO prepared by several synthetic methods.

Great interest in improving the gas sensitivity as well as selectivity and in decreasing the working temperature has been witnessed. Nitrogen dioxide (NO₂) is considered a common air pollutant produced during combustion in automotive engines, industrial factories, and power plants. Therefore, the development of stable NO₂ gas sensors that can detect extremely low concentrations of NO₂ with high sensitivity is highly desirable. In this study, undoped ZnO nanopowders have been prepared by the flame spray pyrolysis process and their gas sensing responses towards different gases have been comparatively examined. In particular, three types of sensors were tested under oxidizing and reducing gases, like nitrogen dioxide, ethanol and sulfur dioxide.

Sensing and characterization of the gas sensing properties

The undoped ZnO sensing film was prepared by mixing the nanoparticles into an organic paste composed of ethyl cellulose and terpineol, which acted as a vehicle binder and solvent, respectively. The resulting paste was spin-coated on Al₂O₃ substrates with predeposited interdigitated Au electrodes. The films were then annealed at 400 °C for 2 h (with heating rate of 2 °C/min) for binder removal. The morphology and the cross section of sensing films were analyzed by SEM. The gas-sensing characteristics of the undoped ZnO nanoparticles towards NO₂, C₂H₅OH and SO₂ were

characterized. The flow through technique was used to test the gas-sensing properties of thin films. A constant flux of synthetic air of 2 L/min was mixed with desired concentrations of pollutants. All measurements were conducted in a temperature-stabilized sealed chamber at 20 °C under controlled humidity. The external NiCr heater was heated by a regulated dc power supply to different operating temperatures. The operating temperature was varied from 200 °C to 350 °C. The resistances of various sensors were continuously monitored with a computer-controlled system by voltage-amperometric technique with 5 V dc bias and current measurement through a picoammeter. The sensor was exposed to a gas sample for ~5 minutes for each gas concentration testing and then the air flux was restored for 15 minutes. The concentration of NO₂, C₂H₅OH and SO₂ were varied from 1 to 50 ppm, 50 to 100 ppm and 10 to 500 ppm, respectively.

EM sensing layer

The cross-section, film thickness, and surface morphology of the undoped ZnO sensing film layer after annealing and sensing test at 300 °C were observed using SEM analysis, as shown in Figure 4. The thickness of sensing film was approximately 10 μm (side view) which benefited tremendously the NO₂, C₂H₅OH and SO₂ gas sensing properties. Irregularities in the film thickness (top view) stem from the spin coating technique. The high density Al₂O₃ substrate interdigitated with Au electrodes was also visible. After the annealing process, a denser film layer was formed. The sensitivity and response time of the thick films of the undoped ZnO nanoparticles as a function of NO₂, C₂H₅OH and SO₂ concentrations at 300 °C. In Figure 5(a), it can be seen that the sensitivity toward NO₂ is increased considerably at 50 ppm NO₂ concentration. The sensitivity and response time for the undoped ZnO nanoparticles at 50 ppm NO₂ concentration were found to be 33 and 7 s, respectively. The sensitivity, however, are decreased considerably by testing the undoped ZnO sensor with C₂H₅OH and SO₂ at 50 ppm concentration of each gas. The sensitivity of 7 and 3 with the response time of 94 and 17 s are obtained at 50 ppm of C₂H₅OH and 50 ppm of SO₂, respectively. It is important to note that the undoped ZnO nanoparticles behave as an n-type semiconductor with decreased resistance during NO₂, C₂H₅OH and SO₂ gas exposure, which is a typical behavior of ZnO material. The gas-sensing sensitivity, S , is defined as the ratio of R_a/R_g where R_a is the resistance in dry air, and R_g is the resistance in test gas. The response time, T_{res} , is defined as the time required until 90% of the response signal is reached. The recovery time, T_{rec} , denotes the time needed until 90% of the original baseline signal is recovered. The sensor behaviors under the operating

temperature of 300 °C versus the NO₂ concentrations ranging from 1–50 ppm for the flame-made undoped ZnO nanoparticles were plotted as shown in Figure 2.1 (a). The changes in resistance of the undoped ZnO sensor for C₂H₅OH and SO₂ gases under exposure to 50–1,000 ppm of C₂H₅OH and 10–500 ppm of SO₂ during forward cycle at 300 °C. It is well known that the sensitivity of a semiconductor gas sensor is highly influenced by its operating temperature. In order to determine the optimum operating temperatures, the response of the undoped ZnO gas sensor to 50 ppm concentration of nitrogen dioxide, ethanol and sulfur dioxide in air was tested as a function of operating temperature. It is clear that the responses of three gases tested varied with operating temperature. The sensitivity to NO₂ first increased with temperature, up to 300 °C, and then gradually decreased. The maximum sensitivity towards NO₂ was 33, at 300 °C. For ethanol and SO₂, the sensitivity continuously increased when operating temperatures varied from 200 to 300 °C, and then decreased. The maximum sensitivities obtained were 7 and 3, at 300 °C. Therefore, optimal operating temperatures of 300 °C were chosen for NO₂, ethanol and SO₂ respectively, to further examine the characteristics of the gas sensor. Results suggest that the undoped ZnO sensor can act as a multifunctional selective gas sensor, detecting NO₂, ethanol and SO₂ gases. In other words, the above mentioned sensor can be used as an excellent NO₂ sensor at an operating temperature of 300 °C.

Gas sensors on zinc oxide nanostructures

Gas sensors based on semiconducting metal oxides are being widely used for sensing gases and vapors. The initial momentum was provided by the findings of Seiyama et al. in metal oxide-gas reaction effects in 1962. It was shown that the electrical conductivity of ZnO can be changed by the presence of reactive gases in the air. The merits of these sensors include their reliability, low cost and easy implementation. Nanostructures of metal oxides have been found to be most effective as gas-sensing materials at elevated temperatures. Very popular sensing materials are metal oxide semiconductors such as ZnO, SnO₂, TiO₂, and WO₃. Generally the change of electric field (conductance, voltage, resistance or the change of piezoelectric effect) of the sensor is monitored as a function of the target gas concentration. Gas sensors normally operate in air, in the presence of humidity and interfering gases. A heated substrate membrane is fitted with gas sensitive nanostructured semiconductor material which generates electrical output signals once chemical reactions are initiated at their surface. A common property of all these detection reactions is that they

require significant levels of thermal activation to proceed at a measurable rate. Nanostructures of semiconducting oxides are widely used for gas sensing due to their large surface area to volume ratio and possibility of complete depletion of carriers within nanostructures when exposed to gases. Nitrogen dioxide (NO₂) is a reddish-brown, highly reactive gas that reacts in the air to form corrosive nitric acid as well as toxic organic nitrates. The major man made source of NO₂ emissions is high-temperature fuel combustion in motor vehicles and industries. These emissions are primarily in the form of NO which gets oxidized in the atmosphere to NO₂. The conversion rate depends on the ambient concentration of NO and O₃. If O₃ is present, the conversion is very rapid. Health and safety guidelines suggest that humans should not be exposed to 3ppm or more NO₂ gas for periods longer than eight hours because of its toxicity. NO₂ is a pulmonary irritant primarily affecting the upper respiratory system in human beings. Continued or frequent exposure to high levels of NO₂ can cause inflammation of the lungs. Therefore, the development of a stable NO₂ gas sensor that can detect extremely low concentrations of NO₂ with high sensitivity and selectivity is highly desirable. Such a sensor can be used for environmental monitoring. It can also be used in an early warning system that detects the presence of NO₂ before the critical concentration of NO₂ is reached. Metal oxides such as SnO₂, WO₃, TiO₂ and ZnO possess high sensitivity to changes in their surrounding atmosphere at elevated temperatures. The sensing properties of metal oxides in form of thick or thin films have been studied to improve, by the addition of noble metals namely Pd, Pt, Au, Ag in terms of selectivity and stability. In 1991, Yamazoe showed that reduction of crystallite size caused a huge improvement in sensor performance. In a low grain size metal oxide almost all the carriers are trapped in surface states and only a few thermal activated carriers are available for conduction. From the point of view of device fabrication, first generation gas sensor devices were fabricated by thick film technology. Then the material fabrication processes improved towards the thin film technology. The fabrication process for thin film technology namely physical and chemical vapour deposition was highly automated and offers high reproducibility. The electrical properties of both thin and thick film sensors drift due to the grain porosity modification and grain boundary alteration. Several methods like addition of noble metals as catalysts or mixed oxides were put forward to improve the sensing performance of the gas sensors. The structural engineering of metal oxide nanostructured thin films proved to optimize the performance of these types of gas sensors. The various operating parameters such as response time, output signal, selectivity and stability can be improved and tuned through the optimization of the structure. Using structural engineering method, the various geometric parameters of metal oxide gas sensing matrix like grain size, agglomeration, film thickness, porosity

can be controlled. The next forward step in gas sensing was achieved by the successful preparation of stable single crystal quasi-one-dimensional semiconducting oxides (nanorods, nanowires) leading to the third generation of metal oxide gas sensors.

3. Objectives

The present work involves the study of MNPs of ZnO by chemical precipitation method, studying growth, microstructure, and morphology and from that correlating the microstructure to its properties. At the beginning, efforts have been made to optimize the precipitation conditions. It is needless to mention that the properties of the MNPs depend extensively on the growth conditions, which influences its microstructure. Different parameters like substrate temperature, PH of solution, deposition time, annealing, ammonia modification etc. were carefully monitored to decide the optimized growth condition of the MNPs. The other objective of this study is to found out the different applications of MNPs of zinc oxide for gas sensor.

4. Need and Scope of MNPs of ZnO

Majority of the research community devoted their work on the wide band gap semiconductors due to wide spectrum of applications in sensors, light emitting diodes, lasers, optical switches, solar cells, light detectors, etc. [65-70]. ZnO is one candidate belonging to the wide band gap semiconductor category, which is II –VI semiconductor having bulk band gap 3.4eV and cubic and hexagonal wurtzite-type crystal structure [68]. It shows size dependent properties like blue shift in band gap [69], nonlinear absorption and scattering [70], low melting point [71], etc. Nanotechnology is derived from the combination of two words Nano and Technology. Nano means very small or “miniature”. So, Nanotechnology is the technology in miniature form. It is the combination of Bio-technology, Chemistry, Physics and Bio-informatics, et Nanotechnology originated in India around 16 years back. It is in its early development phase and therefore the industry keeps a keen watch over the students who pursue M. Tech. in nanotechnology. There are several career opportunities for such students in domestic as well as international markets. This new sphere of scientific innovation has a broader scope. Several Indian institutes have introduced degree courses in Nanotechnology at both the UG and PG levels. The areas covered in the Nanotech are Food and Beverage, Bio-Technology, Forensic Sciences, Genetics, Space Research, Environment industry, Medicine, Agriculture and Teaching. The three chief divisions of Nanotech are Nanoelectronics, Nanomaterials, and Nano-Biotechnology. The implications of Nanotechnology in India can be found

in the field of telecommunications, computing, aerospace, solar energy, and environment. However, Nanotech's major contribution can be seen in the computing, communication and, medical field. Nano- medicine is the most important field of Nanotechnology. The nano level gadgets and materials are used for diagnosing and treatment of diseases. Nano-Pharmacology has generated a specific category of smart drugs that affect negligible side effects. The use of Nanotech has also helped in the detection of narcotics and fingerprints of the suspected criminals. The Council of Scientific and Industrial Research, also known as CSIR has set up 38 laboratories in India dedicated to research in Nanotechnology. This technology will be used in diagnostic kits, improved water filters and sensors and drug delivery. The research is being conducted on using it to reduce pollution emitted by the vehicles. Looking at the progressive prospects of Nanotechnology in India, Nanobiosym Inc., a US-based leading nanotechnology firm is planning to set up India's first integrated nanotechnology and biomedicine technology park in Himachal Pradesh. Nanotechnology has certainly acquired an essential position in the Indian Economy and Scientific Research Department and it is expected to reach the pinnacle of Development thereby making India a role model for the countries of the world. [72]

5. Hypothesis

Zinc oxide (ZnO) is one of the most important semiconducting materials, having a wide range of potential applications. ZnO is an important electronic and photonic material because of its wide direct based gap of 3.37 eV. In recent years, ZnO nanocrystals have been used for solar cell applications, gas sensors and ultraviolet lasing action at room temperature. Nanocrystals of ZnO have been prepared using both physical and chemical methods. Among them sol-gel chemistry, spray pyrolysis, micro emulsion, precipitation solvothermal and hydrothermal methods are being extensively used. Generally, most of these methods of synthesis require relatively high temperatures or involve the use of expensive chemicals or apparatus. It is therefore advisable to find simple methods to produce ZnO nanocrystals using commonly available chemicals. A detailed study of the interaction of alcohols with Zn metal has revealed that the C-O bond of the alcohol is readily cleaved on Zn metal surfaces giving hydrocarbons and the oxidic species on the metal surface. Using this simple technique, we found that ZnO nanocrystals are readily produced by the reaction of zinc metal with ethanol. Addition of ethylenediamine (EDA) to the reaction mixture produces ZnO nanorods, giving evidence of clustering phenomenon.

6. Methods of Synthesis

The MNPs of ZnO can be accomplished by two approaches.

With top-down technology nanostructures and devices are made through scaling and miniaturization. It requires precision engineering down to the nano-scale, usually by lithographic patterning, embossing or imprint techniques with subsequent etching and coating steps. Examples are: micro- and nanoelectronics, MEMS, micro electro mechanical systems, nanostructures such as lotus coatings, catalytic surfaces, and membranes, nanostructured coatings in displays, solar cells, flat Batteries, nanofibers by electrospinning, Nanoclay platelets and tubes by exfoliation

The other complementary route is bottom-up, constructing nanostructures through atom-by-atom or molecule-by molecule engineering. It usually requires wet-chemical or vapor-phase processing routes such as atomic layer deposition. In some cases atomic or molecular manipulation is applied via optical, electrical or mechanical nanopores. Typical examples are: Carbon nanotubes by gas phase deposition, Nanowires made from metal, Metal oxide, ceramic or even polymer type by gas phase deposition, Quantum dots, Self assembling, molecular and Biostructures, Nanomedicine. [57]

7. Research Methodology

1. The MNPs of ZnO will be prepared by simple chemical precipitation method for their application.
2. The particle size will be varied by changing the annealing temperature.
3. The sample will be characterized by Transmission Electron Microscopy (TEM), Atomic force Microscopy (AFM), Scanning electron Microscopy (SEM) and Powder X-ray diffraction to know the particle size.
4. UV-Visible study will be performed to know the nanoparticles confirms increase in the band gap with the decrease in particle size.
5. Photoluminescence study will be caused by energetic optical photons.
6. The experimental data will be analyzed.
7. Conclusions will be drawn and applicability of the material will be decided.

8. Conclusion

MNPs of Zinc oxide have attracted considerable attention due to their unique properties, which are not present in bulk materials. These MNPs exhibit size dependent properties (size quantization effects) such as a blue shift of absorption onset, a change of electrochemical potential of band edge, and an enhancement of photocatalytic activities, with decreasing crystallite size. CdS, in particular,

have been extensively studied due to their potential applications such as field effect transistors, light emitting diodes, photocatalysis and chemical & biological sensors. Many synthetic methods have been employed to prepare MNPs of ZnO including soft chemical reaction, solid-state reaction, sonochemical preparation, microwave heating, photoetching and reverse micelle. In this investigation, we have developed a new method to produce MNPs of ZnO of small sizes using chemical precipitation method.

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