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"MNPs OF ZnO-PREPRATIONS AND CHARACTERIZATION FOR GAS SENSOR APPLICATIONS"

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Abstract

ZnO is a key technological material. 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. ZnO nanostructures are easily formed even on cheap substrates such as glass and hence they have a promising potential in the nanotechnology future. ZnO nanocrystals are also attractive for sensor and biomedical application due to its bio-safety and large surface area. ZnO has some advantages over GaN among which are the availability of fairly high-quality ZnO bulk single crystals and a large exciton binding energy (_60 meV). ZnO also has much simpler crystal-growth technology, resulting in a potentially lower cost for ZnO-based devices. The present work involves study Zinc Oxide nanocrystal material by chemical precipitation method for growth of high quality ZnO nanocrystal material studying microstructure and from that correlating the microstructure to its physical, electrical and optical *properties. At the beginning, efforts have been made to optimize the deposition conditions. It is needless to mention that the properties of the thin films depend extensively on the growth conditions, which influences its microstructure. Different parameters like substrate temperature, PH of solution, deposition time, speed of rotation etc. were carefully monitored.*

1. Introduction

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.

1.1 Chemical properties

ZnO occurs as a white powder. The mineral zincite usually contains manganese and other impurities that confer a yellow to red color. Crystalline zinc oxide is thermochromic, changing from white to yellow when heated and in air reverting to white on cooling. This color change is caused by a small loss of oxygen to the environment at high temperatures to form the non-stoichiometric $Zn_{1+x}O$, where at 800 °C, x = 0.00007.

Zinc oxide is an amphoteric oxide. It is nearly insoluble in water, but it is soluble in (degraded by) most acids, such as hydrochloric acid:

$$ZnO + 2\ HCl \rightarrow ZnCl_2 + H_2O$$

Bases also degrade the solid to give soluble zincates:

$$ZnO + 2\ NaOH + H_2O \rightarrow Na_2[Zn(OH)_4]$$

ZnO reacts slowly with fatty acids in oils to produce the corresponding carboxylates, such as oleate or stearate. ZnO forms cement-like products when mixed with a strong aqueous solution of zinc chloride and these are best described as zinc hydroxy chlorides. This cement was used in dentistry.

1.2 Mechanical properties

ZnO is a relatively soft material with approximate hardness of 4.5 on the Mohs scale. Its elastic constants are smaller than those of relevant III-V semiconductors, such as GaN. The high heat capacity and heat conductivity, low thermal expansion and high melting temperature of ZnO are beneficial for ceramics. ZnO's most stable phase being wurtzite, ZnO exhibits a very long lived optical phonon E2(low) with a lifetime as high as 133 ps at 10 K

Among the tetrahedrally bonded semiconductors, it has been stated that ZnO has the highest piezoelectric tensor, or at least one comparable to that of GaN and AlN. This property makes it a technologically important material for many piezoelectrical applications, which require a large electromechanical coupling.

1.3 Electrical properties

ZnO has a relatively large direct band gap of ~3.3 eV at room temperature. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation. The bandgap of ZnO can further be tuned to ~3–4 eV by its alloying with magnesium oxide or cadmium oxide.

Most ZnO has n-type character, even in the absence of intentional doping. Nonstoichiometry is typically the origin of n-type character, but the subject remains controversial.[22] An alternative explanation has been proposed, based on theoretical calculations, that unintentional substitutional hydrogen impurities are responsible. Controllable n-type doping is easily achieved by substituting

Zn with group-III elements such as Al, Ga, In or by substituting oxygen with group-VII elements chlorine or iodine.

1.4 Nanophase ZnO

Nanophase ZnO can be synthesized into a variety of morphologies including nanowires, nanorods, tetrapods, nanobelts, nanoflowers, nanoparticles etc. Nanostructures can be obtained with most above-mentioned techniques, at certain conditions, and also with the vapor-liquid-solid method.

Rodlike nanostructures of ZnO can be produced via aqueous methods, which are attractive for the following reasons: They are low cost, less hazardous, and thus capable of easy scaling up; the growth occurs at a relatively low temperature, compatible with flexible organic substrates; there is no need for the use of metal catalysts, and thus it can be integrated with well-developed silicon technologies. In addition, there are a variety of parameters that can be tuned to effectively control the morphology and properties of the final product. Wet chemical methods have been demonstrated as a very powerful and versatile technique for growing one dimensional ZnO nanostructures. The synthesis is typically carried out at temperatures of about 90 °C, in an equimolar aqueous solution of zinc nitrate and hexamine, the latter providing the basic environment. Certain additives, such as polyethylene glycol or polyethylenimine, can improve the aspect ratio of the ZnO nanowires.[32] Doping of the ZnO nanowires has been achieved by adding other metal nitrates to the growth solution. The morphology of the resulting nanostructures can be tuned by changing the parameters relating to the precursor composition (such as the zinc concentration and pH) or to the thermal treatment (such as the temperature and heating rate).

1.5 Applications of Zinc Oxide

The applications of zinc oxide powder are numerous, and the principal ones are summarized below. Most applications exploit the reactivity of the oxide as a precursor to other zinc compounds. For material science applications, zinc oxide has high refractive index, high thermal conductivity, binding, antibacterial and UV-protection properties. Consequently, it is added into materials and products including plastics, ceramics, glass, cement, rubber, lubricants, paints, ointments, adhesive, sealants, pigments, foods, batteries, ferrites, fire retardants, etc.

i) Rubber manufacture

About 50% of ZnO use is in the rubber industry. Zinc oxide along with stearic acid is used in the vulcanization of rubber ZnO additive also protect rubber from fungi and UV light.

ii) Concrete industry

Zinc oxide is widely used for concrete manufacturing. Addition of ZnO improves the processing time and the resistance of concrete against water.

iii) Medical

Zinc oxide as a mixture with about 0.5% iron(III) oxide (Fe_2O_3) is called calamine and is used in calamine lotion. There are also two minerals, zincite and hemimorphite, which have been historically called calamine. When mixed with eugenol, a ligand, zinc oxide eugenol is formed, which has applications as a restorative and prosthodontic in dentistry.

Reflecting the basic properties of ZnO, fine particles of the oxide have deodorizing and antibacterial properties and for that reason are added into materials including cotton fabric, rubber, and food packaging. Enhanced antibacterial action of fine particles compared to bulk material is not intrinsic to ZnO and is observed for other materials, such as silver. This property is due to the increased surface area of the fine particles.

Zinc oxide is widely used to treat a variety of other skin conditions, in products such as baby powder and barrier creams to treat diaper rashes, calamine cream, anti-dandruff shampoos, and antiseptic ointments. It is also a component in tape (called "zinc oxide tape") used by athletes as a bandage to prevent soft tissue damage during workouts.

Zinc oxide can be used in ointments, creams, and lotions to protect against sunburn and other damage to the skin caused by ultraviolet light (see sunscreen). It is the broadest spectrum UVA and UVB reflector that is approved for use as a sunscreen by the FDA, and is completely photostable. When used as an ingredient in sunscreen, zinc oxide sits on the skin’s surface and is not absorbed into the skin, and blocks both UVA (320–400 nm) and UVB (280–320 nm) rays of ultraviolet light. Because zinc oxide (and the other most common physical sunscreen, titanium dioxide) are not absorbed into the skin, they are nonirritating, nonallergenic, and non-comedogenic.

Many sunscreens use nanoparticles of zinc oxide (along with nanoparticles of titanium dioxide) because such small particles do not scatter light and therefore do not appear white. There has been concern that they might be absorbed into the skin, and a study published in 2010 found that nanoparticles of ZnO that were applied to human skin via sunscreens could be traced in venous blood and urine samples. In contrast, a comprehensive review of the medical literature from 2011 says that no evidence of systemic absorption can be found in the literature.

iv) Cigarette filters

Zinc oxide is a constituent of cigarette filters for removal of selected components from tobacco smoke. A filter consisting of charcoal impregnated with zinc oxide and iron oxide removes significant amounts of HCN and H_2S from tobacco smoke without affecting its flavor.

v) Food additive

Zinc oxide is added to many food products, including breakfast cereals, as a source of zinc, a necessary nutrient. (Zinc sulfate is also used for the same purpose.) Some prepackaged foods also include trace amounts of ZnO even if it is not intended as a nutrient.

vi) Pigment

Zinc white is used as a pigment in paints and is more opaque than lithopone, but less opaque than titanium dioxide. It is also used in coatings for paper. Chinese white is a special grade of zinc white used in artists' pigments. It is also a main ingredient of mineral makeup.

vii) Coatings

Paints containing zinc oxide powder have long been utilized as anticorrosive coatings for metals. They are especially effective for galvanized iron. Iron is difficult to protect because its reactivity with organic coatings leads to brittleness and lack of adhesion. Zinc oxide paints retain their flexibility and adherence on such surfaces for many years.

2. Literature Review

In the last two decades different means of modification of synthetic fibres have been thoroughly explored. The increasing expectancy for smart materials in daily life has of late sharply influenced research in the area of modification. Technologies that involve engineering to convert inexpensive materials into valuable finished goods have become more important in the present scenario.

Functionalisation of textile polymers has been practiced by different techniques to confer new properties on to the fibre so as to enable their application in fields other than textile industry. The functionalities of fibres like anti-static, anti-bacterial, anti-odor, soil-resistance, biocompatibility etc. are function of fiber surface properties independent of characteristics of the fiber bulk. Development of processes for imparting these functionalities to the textile substrates is of prime importance.

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.

2.1. Particle synthesis and characterization

Zinc naphthenate (Aldrich, 8 wt% Zn) was used as a precursor. The precursor was dissolved in xylene (Carlo Erba, 98.5%) to obtain a 0.5 mol/L precursor solution. In a typical run, the precursor was fed into a FSP reactor by a syringe pump with a rate of 5 mL/min while 5 L/min O_2 was being dispersed (5/5 flame). The gas flow rates of methane and O_2 supporting flamelets were 1.19 and 2.46 L/min, respectively. The pressure drop at the capillary tip was kept constant at 1.5 bars by adjusting the orifice gap area at the nozzle.

The flame height was observed to be approximately 10–12 cm. The sample showed a yellowish-orange flame. The liquid precursor mixture was rapidly dispersed by a gas stream and ignited by a premixed methane/oxygen flame. After evaporation and combustion of precursor droplets, particles are formed by nucleation, condensation, coagulation and coalescence. Finally, the nanoparticles were collected on glass microfiber filters with the aid of a vacuum pump. The undoped ZnO nanopowders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Specific surface area (SSA_{BET}) of the nanoparticles was also investigated by nitrogen adsorption (BET analysis).

2.2. 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 Al_2O_3 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 NO_2, C_2H_5OH and SO_2 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 NO_2, C_2H_5OH and SO_2 were varied from 1 to 50 ppm, 50 to 100 ppm and 10 to 500 ppm, respectively.

2.2.1 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 NO_2, C_2H_5OH and SO_2 gas sensing properties. Irregularities in the film thickness (top view) stem from the spin coating technique. The high density Al_2O_3 substrate interdigitated with Au electrodes was also visible. After the annealing process, a denser film layer was formed.

2.3 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.

2.3.1 Working principle of metal oxide gas sensors

Conductometric metal oxide gas sensors depend on changes of electrical conductivity due to the interaction with the surrounding atmosphere. The normal operating temperature of metal oxide gas sensors is within the range between 200 °C and 500 °C. The operating temperature should be high enough so that gas reactions occur in a time on the order of the desired response time and should also be low enough to avoid any variations in the bulk of the sensing matrix. The single crystal structure synthesized at temperatures higher than the operating temperature of the sensor shows high stability.

Based on the study of a large range of oxides, the phenomenon of change in conductivity to the presence of reactive gases in air is common to oxides and not specific to a few special cases. If the conductivity is too high, then an effect is not expected and similarly if the conductivity is too low, then an effect will be difficult to measure. In practical applications, if an oxide sample has a resistivity between 104 and 108 Ocm at 300- 400 °C, then it will function as a gas sensor when heated to a temperature in this range.

2.3.2 Sensor Characteristics

The characteristic of a sensor is classified into static and dynamic. Static characteristics can be measured when all the transient effects of the output signal have stabilized in to steady state. Dynamic characteristics tend to describe the sensor's transient behavior.

A) Static characteristics

a) Sensitivity

Sensitivity is the ratio of incremental change in the output of the sensor to its incremental change of the measurand in input. For example, if we have a gas sensor whose output voltage increases by 1 V when the oxygen concentration increases by 1000 ppm, then the sensitivity would be 1 mV/ppm. Generally, the sensitivity to the target gas is defined as the percent reduction of sensor resistance.

Sensitivity (%) = [(Ra- Rg) / Ra] ×100,

where Ra is the value of initial equilibrium resistance in air and Rg is resistance in the presence of a target gas. For convenience sometimes the sensitivity of gas sensor is expressed as the ratio of resistance in air over resistance in gas for reducing gases (Ra/Rg) and resistance in gas over resistance in air (Rg/Ra) for oxidizing gas.

b) Selectivity

The sensor's ability to measure a single component in the presence of others is known as its selectivity. For example, an oxygen sensor that does not show a response to other gases such as CO, CO2 is considered to be selective.

Selectivity = (sensitivity of gas1/sensitivity of gas2)

Selectivity of the sensor is assessed by the ratio of sensitivity between the gases that is of interest to be detected over the gases that are uninteresting for detection in equivalent concentrations. To improve selectivity to specific gases, sensor array technology is also being adapted.

c) Stability and Drift

The sensor's ability to produce the same output value when measuring a fixed input over a period of time is termed as stability. Drift is the gradual change in the sensor's response characteristics while the input concentration of the gas remains constant. Drift is the undesired and unexpected change that is unrelated to the input. It may be attributed to aging, temperature instability, contamination, material degradation, etc. For instance, in a gas sensor, gradual change of temperature may change the baseline stability, or gradual diffusion of the electrode's metal into substrate may change the conductivity of a semiconductor gas sensor.

d) Repeatability

It denotes the sensor's ability to produce the same response for successive measurements of the same input, when all operating and environmental conditions remain constant.

e) Reproducibility

The sensor's ability to reproduce responses after some measurement condition has been changed. For example, after shutting down a sensing system and subsequently restarting it, a reproducible sensor will show the same response to the same measure and concentration as it did prior to being shut down.

f) Hysteresis

It is the difference between output readings for the same measure and, when approached while increasing from the minimum value and the other while decreasing from the peak value.

2.3.4 Influence of contact electrodes on sensor performance

The contact electrodes used in gas sensors can have both electrical and electrochemical roles. For thin compact films, contact resistance plays an important role as dominant factor in overall resistance. The contribution of contact resistance is also extremely important for the case in which individual nanorods, nanowires or nanobelts are used as sensing layers. These electrodes are generally made of metals. They can also be fabricated from materials such as conductive polymers or conductive metal oxides.

Although the concept of resistance change of the sensitive material when exposed to target gas is widely known, the overall resistance of the sensor depends not only on the gas sensing material properties but also on parameters such as transducer morphology, electrode etc. When the sensitive layer consists only of a compact continuous material and the thickness is larger than the Debye length, it can only partly depleted when exposed to target gas. In this case, the interaction does not influence the entire bulk of the material. Two levels of resistance are established in parallel and this fact limits the sensitivity. Thin layer will be the better choice which can be fully depleted.

The representation shows the influence of electrode-sensing layer contacts. Rc is resistance of the electrode-metal oxide contact, R11 is the resistance of the depleted region of the compact layer, R1 is the equivalent of series resistance of R11 and Rc, and the equivalent series resistance of SRgi and Rc, in the porous and compact situations, respectively. Rgi is the average inter-grain resistance in the case of porous layer, Eb minimum of the conduction band in the bulk, qVs band bending associated with surface phenomena on the layer, and qVc also contains the band bending induced at the electrode-metal oxide contact.

2.3.5 Improvement of selectivity by surface modifications

Mixing metal oxides with

a. Metals that function as catalysts

b. Binary compounds and multi-component materials

c. Doping

The most common methods used to enhance the gas sensing performance of metal oxide gas sensors. These additives can be used for modifying the catalytic activity of the base oxide, favoring formation of active phases and improving the electron exchange rate. The interaction of gas with the sensing material, resulting in the gas sensitivity, is determined by the chemical properties of the sensor surface. Different surface atoms can be introduced on the surface of the metal oxide sensors. This surface modification leads to new chemical reactivity and enables the sensor to be operated at low temperatures.

Nanoscale particles of noble metals (Pd, Pt, Au and Rh) and oxides of other elements (Co, Cu and Fe) deposited on the surface of metal oxides can act as surface sites for adsorbates and promoters for surface catalysis. They create additional adsorption sites and surface electronic states and as a result gas sensitivity, selectivity, rate of response can be altered. For achieving high gas response, the noble metal should create optimal conditions for both electron and ion (spillover) exchange between surface and reacting gas species.

2.3.6 Improvement of selectivity by operating conditions

The sensor material may be operated at a comparably wide range of operating temperatures (300 - 900 C) leading to different thermal energies for the surface reactions, differences may be attained by selecting the operating temperature, leading to a variation in gas sensitivity. A more improved version of this idea is to continuously increase or decrease the operating temperature of a given sensor and to continuously measure the variation of conductivity. This technique is known as temperature transient operation which gives more information in case of gas mixtures. To realize selective gas detection, sensor arrays are also constructed where several sensors showing different patterns of gas sensitivity are selected and simultaneously operated. A simple technique to obtain an array using one sensor is to modulate the operating temperature to different levels. Excessive increase of operating temperature may lead to a considerable drop of gas sensitivity. Moreover increasing working temperature can create conditions, where gas response will then be determined by change of bulk properties of material.

2.3.7 Improvement of response and recovery time of gas sensors

A high speed gas switching system can be used to improve the response of the gas sensor. Yamazoe et al. studied the response and recovery properties of $SnO2$ porous film gas sensors using a high speed gas switching system. The developed system allows the rapid replacement of the gas atmosphere in the chamber between air and $H2$ (or CO). It was reported that the response speed of the sensor was fast, reaching a response time of less than 0.5s at 350 C. The rates of diffusion and surface reactions of these gases ($H2$ and CO) in the porous sensing film are high enough for the sensor to reach a steady state within a short time. However the resistance in air did not reach the original value by repeated switching. This incomplete recovery was attributed to the slow desorption of $H2O$ and $CO2$ formed on $SnO2$ by the surface reaction of $H2$ and CO respectively.

2.3.8 Metal oxide nanostructure based conductometric gas sensors

Zinc oxide

Characterization of gas sensing properties of ZnO nanowires is reported by Ahn et.al. ZnO nanowires were fabricated by a selective growth method on patterned Au catalysts forming a nanobridge between two Pt pillar electrodes. The gas sensing properties were demonstrated using

NO2 gas. The response as a function of temperature is shown to be highest at 225 C and linearly increased with the concentration of NO2 in the range of 0.5 - 3ppm and saturated beyond this range. The sensor performance is also compared with ZnO nanocrystals, Sn and In doped ZnO thin film. Also the nanobridge structure is shown to have fast recovery behaviour because the desorbed gas molecules can be easily removed off from the nanowires surfaces.

Lupan et.al demonstrated the gas sensing behaviour of Al doped ZnO films synthesized by successive chemical deposition method. Successive chemical solution deposition method was reported to be simple and requires non-sophisticated equipment to produce nanostructures with high efficiency. Nanostructured ZnO films doped with Al showed a high sensitivity to CO2 than undoped ZnO films.

Characterization and gas sensing properties of ZnO hollow spheres is reported by Zhang et.al. Different concentrations of NH3 and NO2 at different temperatures were used to test the gas sensor. ZnO hollow sphere sensor exhibited extremely different sensing behaviors to NH3 and NO2. The optimum operating temperature of the sensor was 200 C for NH3 and 240 C for NO2 respectively. The gas sensor exhibited much higher response to NO2 than to other gases at 240 C implying good selectivity and potential application of the sensor for detecting NO2.

2.4 Metal Oxide Gas Sensors: Sensitivity and Influencing Factors

Conductometric semiconducting metal oxide gas sensors have been widely used and investigated in the detection of gases. Investigations have indicated that the gas sensing process is strongly related to surface reactions, so one of the important parameters of gas sensors, the sensitivity of the metal oxide based materials, will change with the factors influencing the surface reactions, such as chemical components, surface-modification and microstructures of sensing layers, temperature and humidity.

The conductometric semiconducting metal oxide gas sensors currently constitute one of the most investigated groups of gas sensors. They have attracted much attention in the field of gas sensing under atmospheric conditions due to their low cost and flexibility in production; simplicity of their use; large number of detectable gases/possible application fields. In addition to the conductivity change of gas-sensing material, the detection of this reaction can be performed by measuring the change of capacitance, work function, mass, optical characteristics or reaction energy released by the gas/solid interaction. As a simple review of metal oxide gas sensors, the main attention in this paper will be focused on the conductometric semiconducting metal oxide gas sensors (especially surface conductive metal oxide).

2.4.1 Metal Oxides for Gas Sensors

Many metal oxides are suitable for detecting combustible, reducing, or oxidizing gases by conductive measurements. The following oxides show a gas response in their conductivity: Cr_2O_3, Mn_2O_3, Co_3O_4, NiO, CuO, SrO, In_2O_3, WO_3, TiO_2, V_2O_3, Fe_2O_3, GeO_2, Nb_2O_5, MoO_3, Ta_2O_5, La_2O_3, CeO_2, Nd_2O_3. Metal oxides selected for gas sensors can be determined from their electronic structure. The range of electronic structures of oxides is so wide that metal oxides were divided into two the following categories:

- Transition-metal oxides (Fe_2O_3, NiO, Cr_2O_3, *etc.*)
- Non-transition-metal oxides, which include (a) pre-transition-metal oxides (Al_2O_3, *etc.*) and (b) post-transition-metal oxides (ZnO, SnO_2, *etc.*).
- Pre-transition-metal oxides (MgO, *etc.*) are expected to be quite inert, because they have large band gaps. Neither electrons nor holes can easily be formed. They are seldom selected as gas sensor materials due to their difficulties in electrical conductivity measurements. Transition-metal oxides behave differently because the energy difference between a cation d^n configuration and either a d^{n+1} or d^{n-1} configurations is often rather small . They can change forms in several different kinds of oxides. So, they are more sensitive than pre-transition-metal oxides to environment. However, structure instability and non-optimality of other parameters important for conductometric gas sensors limit their field of application. Only transition-metal oxides with d^0 and d^{10} electronic configurations find their real gas sensor application. The d^0 configuration is found in binary transition-metal oxides such as TiO_2, V_2O_5, WO_3. d^1 configuration is found in post-transition-metal oxides, such as ZnO, SnO_2.

2.4.2 Factors Influencing the Sensitivity

Semiconducting metal oxides have been investigated extensively at elevated temperatures for the detection of simple gases. There are many parameters of materials for gas sensor applications, for example, adsorption ability, catalytic activity, sensitivity, thermodynamic stability, *etc.* Many different metal oxide materials appear favorable in some of these properties, but very few of them are suitable to all requirements. For this situation, more recent works focus on composite materials, such as SnO_2-ZnO Fe_2O_3-ZnO , ZnO-CuO *etc.* In addition to binary oxides, there are numerous ternary, quaternary and complex metal oxides, which are of interest of mentioned applications. The combination of metal oxides and other components, for example, organic and carbon nanotubes, were also investigated much. Herein, we mainly take composite metal oxides as examples to introduce the influence of chemical composition.

2.4.3 Surface Modification by Noble Metal Particles

In many gas sensors, the conductivity response is determined by the efficiency of catalytic reactions with detected gas participation, taking place at the surface of gas-sensing material. Therefore, control of catalytic activity of gas sensor material is one of the most commonly used means to enhance the performances of gas sensors. However, in practice, the widely used gas sensing metal oxide materials such as TiO_2, ZnO, SnO_2, Cu_2O, Ga_2O_3, Fe_2O_3, are the least active with catalytic point of view. The pure SnO_2 thin film without any catalyst exhibits a very poor sensitivity (~3) confirming this statement.

2.4.4 Microstructure

The operating characteristics of solid state gas sensors are determined by both receptor and transducer functions. The last function is very important, because it determines the efficiency of chemical interactions' conversion into electrical signal. Therefore, it is very important to synthesize metal oxides with optimal morphology and crystallographic structure.

2.4.5 Humidity and Temperature

Environmental humidity is an important factor influencing the performance of metal oxide gas sensors, as many humidity gas sensors based on metal oxides have been developed. However, mechanism of sensing water vapor and other pollution gas such as CO, NO_2, H_2S, is different. For metal oxide humidity gas sensors, ionic-type humidity sensors are the most common patterns. The conduction mechanism depends on H^+ or H_3O^+, from dissociation of adsorption water, which hops between adjacent hydroxyl groups. Details about the adsorption of water on metal oxide surfaces and mechanism of sensing water vapor can be seen in. Water adsorbing on the metal oxide surface will not donate electrons to sensing layers.

3. Objectives

This study is focused on the literature review of metal oxide based semiconducting zinc oxide non-structures used for gas sensing. The working principle of metal oxide gas sensors, measurement methods and synthesis mechanisms is included in this study.

The main objective of this study is to detect the gas sensing for non-structured zinc oxide for different applications.

4. Hypotheses

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, microemulsion, 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.

5. Zinc Oxide Nanostructures: Synthesis and Properties

Zinc oxide (ZnO), a wide bandgap (3.4 eV) *II-VI* compound semiconductor, has a stable wurtzite structure with lattice spacing a = 0.325 nm and c = 0.521 nm. It has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics.1-10 Invisible thin film transistors (TFTs) using ZnO as an active channel have achieved much higher field effect mobility than amorphous silicon TFTs.

5.1 Synthesis of ZnO Nanostructures

Vapor Transport Synthesis

The most common method to synthesize ZnO nanostructures utilizes a vapor transport process.

In such a process, Zn and oxygen or oxygen mixture vapor are transported and react with each other, forming ZnO nanostructures. There are several ways to generate Zn and oxygen vapor.

Decomposition of ZnO is a direct and simple method, however, it is limited to very high temperatures (~1400°C). Another direct method is to heat up Zn powder under oxygen flow. This method facilitates relative low growth temperature (500~700°C), but the ratio between the Zn vapor pressure and oxygen pressure needs to be carefully controlled in order to obtain desired ZnO nanostructures. It has been observed that the change of this ratio contributes to a large variation on the morphology of nanostructures. The indirect methods to provide Zn vapor include metal-organic vapor phase epitaxy, in which organometallic Zn compound, diethyl-zinc for example, is used under appropriate oxygen or N2O flow. Also in the widely used carbothermal method, ZnO powder is mixed with graphite powder as source material. At about 800-1100 °C, graphite reduces ZnO to form Zn and CO/CO2 vapors. Zn and CO/CO2 later react and result in ZnO nanocrystals. The advantages of this method lie in that the existence of graphite significantly lowers the decomposition temperature of ZnO.

5.2 Other Synthesis Methods

Although the vapor transport process is the dominant synthesis method for growing semiconducting nanostructures such as ZnO, GaN and Si nanowires, other growth methods such as electrodeposition, sol-gel, polymer assisted growth, *etc.* have been developed in parallel. These methods provide the possibility of forming ZnO nanostructures at low temperature. For example, in an electrodeposition method, AAM with highly ordered nanopores was used as a template, zinc nanowires were fabricated into the nanopores via electrodeposition, forming zinc nanowires array, then the nanowire array was oxidized at 300 °C for 2 hours and ZnO nanowire array was obtained.

5.3 Zinc oxide applications

Zinc oxide is a unique material that exhibits semiconducting and piezoelectric dual properties. Using a solid–vapour phase thermal sublimation technique, nanocombs, nanorings, nanohelixes/nanosprings, nanobelts, nanowires and nanocages of ZnO have been synthesized under specific growth conditions.

5.3.1 World Wide use

World-wide use of zinc oxide is in excess of 1.2 million tonnes annually. On a contained zinc basis the oxide accounts for about 9% of metallic zinc. Probably 60% of zinc oxide uses secondary zinc, primarily top dross from continuous galvanising, as the zinc source. China is by far the dominant supplier and also largest user, followed by the U.S.. Although rubber products and in particular tires are the major use for rubber, there are considerable variations around the world in use patterns. For example the ceramic market is equally as important as rubber in some areas. Oil additive compounds are dominated by manufacture within the U.S.

5.3.2 Zinc oxide particles for production of antimicrobial textiles

The application of nanoscale materials and structures, usually ranging from 1 to 100 nanometers (nm), is an emerging area of nanoscience and nanotechnology. Synthesis of noble metal nanoparticles for applications such as catalysis, electronics, textiles, environmental protection, and biotechnology is an area of constant interest. Recently, an awareness of general sanitation, contact disease transmission, and personal protection has led to the development of antimicrobial textiles. The development of antimicrobial cotton fabrics using Zinc oxide nanoparticles has been investigated in this present work. The ZnO nanoparticles were prepared by wet chemical method and were directly applied on to the 100% cotton woven fabric using pad-dry-cure method.

5.3.3 Zinc Oxide: Applications and Market Opportunities by NanoMarkets

NanoMarkets is a leading provider of market and technology research and industry analysis services for the thin film, organic and printable electronics businesses (which we refer to as TOP Electronics.) Since the firm's founding, NanoMarkets has published over two dozen comprehensive research reports on emerging technology markets. Topics covered have included sensors, displays, OLEDs, HB-LEDs, e-paper, RFID, photovoltaics, smart packaging, novel battery technologies, printed electronics, organic electronics, emerging memory and storage technologies and other promising technologies. Our client roster is a who's who of companies in specialty chemicals, materials, electronics applications and manufacturing.

5.3.4 Applications of ZnO as a Conductor

Most of the present applications for ZnO are as a conductive film. As research continues to refine the processes for manufacturing ZnO as a thin film it is becoming clear that this inexpensive abundant material may be suited for a number of applications. Without doubt, displays are the leading application where ZnO is being used as a replacement conductive material.

5.3.5 Applications of ZnO as a Semiconductor and Other Applications

Some of the potential applications for ZnO as a conductor also lend themselves to ZnO as a semiconductor. These include photovoltaics and LEDs, which could become favorable applications for ZnO as a semiconductor. However, there are technical difficulties still being worked out for ZnO. With regard to photovoltaics, the band gap leaves little of the solar spectrum to be absorbed. Since the semiconductors are transparent to light with energy less than the band gap, they only absorb photons with energy greater than the band gap. ZnO has a bandgap of 3.37 eV leaving very little of the solar spectrum able to be absorbed.

5.3.6 Zinc Oxide for Destruction of Tumor Cells and for Drug Delivery

Nanotechnology represents a new and enabling platform that promises to provide a broad range of novel uses and improved technologies for biological and biomedical applications. One of the reasons behind the intense interest is that nanotechnology permits the controlled synthesis of materials where at least one dimension of the structure is less than 100 nm. This ultra-small size is comparable to naturally occurring proteins and biomolecules in the cell [1], and is notably smaller than the typical diameter (~7 μm) of many human cells. The reduction of materials to the nanoscale can frequently alter their electrical, magnetic, structural, morphological, and chemical properties enabling them to interact in unique ways with cell biomolecules and enable their physical transport into the interior structures of cells.

5.3.7. Toxicology concerns of ZnO nanoparticles

Although nanoparticles of many different types of materials can be produced, compatibility issues with living cells limits the types of nanomaterials under consideration for use in biomedical applications. ZnO is considered to be a "GRAS" (generally recognized as safe) substance by the FDA. However, the GRAS designation most commonly refers to materials in the micron to larger size range, as even these substances when reduced to the nanoscale can develop new actions of toxicity. As a result, a detailed evaluation of nanomaterial toxicity in both *in vitro* and *in vivo* systems is needed, as well as identifying means to reduce unwanted toxicity. One common approach to increase biocompatibility and reduce particle aggregation involves coating nanoparticles with discrete sized polymers to render them less toxic, more likely to be taken up by cells, and potentially more suitable for drug delivery applications.

5.3.8. Nanoparticles and Cancer Treatment

The use of nanomaterials as pharmaceutical carriers to enhance *in vivo* anti-tumor efficacy has been considered for more than 30 years. The first studies on the clinical potential of nano-drug carriers as liposomes occurred in the mid-1970's where treatment of tumor bearing mice with liposome-entrapped actinomycin D was shown to significantly prolong survival. Today, the use of nanomaterials for delivery of pharmaceutical and diagnostics agents remains at the forefront of nanomedicine, where recent improvements have been described by conjugating cell specific ligands to the surface of nanoparticles resulting in greater control of drug targeting at the tissue and cellular levels, and by encapsulating drugs within nanoparticles to significantly improve drug release profiles.

5.3.9 ZnO for Biomedical and Cancer Applications

ZnO is a conventional wide band-gap semiconductor that has been highly explored in multiple areas of science. ZnO nanomaterials have been used as semiconductors in microelectronic devices and for accelerating degradation of water pollutants via photocatalytic activity. Due to its inherent ability to absorb UV irradiation and optical transparency, ZnO nanoparticles are used in the cosmetic industry, typically in sunscreens and facial creams. Their recognized antibacterial properties are also encouraging a variety of antimicrobial applications . ZnO nanoparticles have gained interest in other biomedical applications based on their high stability, inherent photoluminescence properties which can be useful in biosensing applications, and wide band-gap semiconductor properties useful in photocatalytic systems and promotion of reactive oxygen species generation.

5.3.10 ZnO Nanoparticles and Cancer Cell Cytotoxicity

Several studies have suggested an increase in *in vitro* cytotoxicity with nanophase ZnO compared to micron-sized ZnO for several types of cancers including glioma, breast, bone, colon, and leukemias and lymphomas .In most of these studies, however, a systematic review of cancer cell cytotoxicity compared to relevant non-immortalized cell types was not performed. Perhaps the most compelling evidence of ZnO preferential toxicity comes from controlled studies comparing nanoparticle susceptibility of cancerous cells to primary non-immortalized cells of identical lineage.

5.3.11 Metal Oxide Nanoparticles and Tumor Imaging and Early Cancer Detection

Interest is growing regarding the use of ZnO and other metal oxide nanomaterials for use as biomarkers for cancer diagnosis, screening, and imaging. Recent studies have shown that ZnO nanoparticle cores capped with polymethyl methacrylate are useful in the detection of low abundant biomarkers. These nanobeads work by facilitating surface absorption of peptide/proteins from cell extracts enabling increased sensitivity and accuracy of cancer biomarker detection using mass spectrometry. Using another approach, a ZnO nanorod-based cancer biomarker assay has been developed for high-throughput detection of ultralow levels of the telomerase activity for cancer diagnosis and screening.

5.4. Metal Oxide Nanoparticles and Targeted Gene Delivery

Nanoparticles are also being studied for use as vehicles for targeted gene delivery to tumor sites. One of the advantages of this approach is that the enclosure of the expression plasmid, or conjugation/absorption of the nucleic acid to the nanoparticle surface ensures safe and efficient gene delivery to the desired tissue. Another advantage relies on the capability of nanoparticles to be taken up by specific cells and internalized to the nucleus according to their surface chemistry. The feasibility of this approach has been validated by a growing number of studies including the reported *in vivo* studies demonstrating inhibition of metastasis in melanoma tumor bearing mice treated with poly-L-lysine modified iron oxide nanoparticles carrying the NM23-H1 gene.

5.4.1 ZnO Nanoparticles and Proinflammatory Cytokines

ZnO nanoparticle exposure has been shown to induce the production of a variety of pro-inflammatory cytokines, including TNF-α, IFN-γ and IL-12, in *in vitro* and *in vivo* pulmonary inhalation studies.The ability of ZnO nanoparticles to induce pro-inflammatory cytokines at nanoparticle concentrations below those causing appreciable cell death suggests that, when used at appropriate concentrations, they could enhance tumor cell killing through the production of TNF-α (tumor necrosis factor), a cytokine named for its potent anti-tumor activities . Nanoparticle-induced cytokines could also facilitate effective anti-cancer actions by eliciting a cytokine profile crucial for directing the development of Th1-mediated immunity. The Th1 lymphocyte subset plays an essential role in enhancing the natural cytotoxic potential of natural killer cells and T cytotoxic cells against cancer cells.

5.5 Properties and novel devices

5.5.1 Luminescent property

ZnO exhibits a direct band-gap of 3.37 eV at room temperature with a large exciton energy of 60 meV. The strong exciton binding energy, which is much larger than that of GaN (25 meV), and the thermal energy at room temperature (26 meV) can ensure an efficient exciton emission at room temperature under low excitation energy. As a consequence, ZnO is recognized as a promising photonic material in the blue–UV region. Single-crystalline ZnO nanowires have been synthesized using high temperature VLS growth methods. Room temperatureUV lasing in ZnO nanowires has been demonstrated.

5.5.2Field effect transistor

Field effect transistors have been fabricated using individual nanobelts. Large bundles of either SnO2 or ZnO nanobelts were dispersed in ethanol by ultrasonication until mostly individual nanobelts were isolated. These ethanol dispersions were dried onto a SiO2/Si substrate for imaging by non-contact mode atomic force microscopy (AFM). SnO2 field effect transistors were fabricated by depositing SnO2 nanobelt dispersions onto SiO2/Si*(*p+*)* substrates; this was followed by treatment in an oxygen atmosphere at 800 ◦C for 2 h. The SiO2/Si substrates were then spin coated with PMMA, baked, exposed to electron-beam lithography for the definition of electrode arrays and developed.

5.5.3 Tunable electrical properties

The conductivity of a nanobelt can be tuned by controlling its surface and volume oxygen deficiency . Before electrical measurement, SnO2 nanobelts are annealed in 1 atm oxygen environment at 800 ◦C for 2 h. Without this treatment, the as-produced nanobelts exhibit no measurable conductivity for

source–drain biases from −10 to 10 V and for gate biases from −20 to 20 V, while after this treatment the SnO2 nanobelts exhibit considerable conductivity. By further annealing of the devices at lower temperatures in vacuum, oxygen or *ambient* the
electrical properties of the nanobelts can be tuned.

5.5.4 Photoconductivity

Ultraviolet light irradiation of the nanobelt diode of SnO2 in air is observed to result in a significant increase of the conductivity (figure 21). Light with a wavelength of 350 nm ($E\lambda$ = 3.54 eV) was used, exceeding the direct band-gap of SnO2. The increase in the conductivity results from both photogeneration of electron–hole pairs as well as doping by UV light induced surface desorption . These processes could be observed by introducing a shutter between the light source and the SnO2 nanobelt so that the flux of UV photons could be turned on and off. The unique geometrical shape of nanobelts is ideal for field emission. MoO3 nanobelts have been shown to exhibit superior performance. The work function at the tips of individual ZnO nanobelts has been measured by a novel technique.

5.5.5 Gas, chemical and biosensors

Conductometric metal oxide semiconductor thin films are the most promising devices among solid state chemical sensors, due to their small dimension, low cost, low power consumption, on-line operation and high compatibility with microelectronic processing. The fundamental sensing mechanism of metal oxide based gas sensors relies on a change in electrical conductivity due to the process of interaction between the surface complexes such as O−, O− 2 , H+ and OH− reactive chemical species and the gas molecules to be detected.

5.5.6 Thermal conductivity

Heat transport at the nanoscale is a very interesting and technologically important area. With the reduction of object size, phonon modes and phonon densities of states change drastically, resulting in unusual thermal transport phenomena in mesoscopic systems.

Conclusion

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. ZnO is a good conductor because of its environmental stability, low resistivity and high transparency, not to mention its low cost and abundance.

The gas sensing process is strongly related to the surface reactions. Different metal oxide based materials have different reaction activation to the target gases. Moreover, good catalyst supporting materials are also a key point to determine how much potential of catalysts can be developed. So, the structure of metal oxide layers is very important. High surface areas are necessary to obtain highly-dispersed catalyst particles. The optical properties of the grown ZnO nanorods were investigated by a time resolved photoluminescence spectroscopy. The results show that the effective decay time of the near bandgap recombination in the CBD grown ZnO nanorods strongly depends on the diameter of the ZnO nanorods. Furthermore, high surface areas can provide large reaction contact area between gas sensing materials and target gases. Porous structure with high surface areas seems to be the standard structure of metal oxide gas sensor layers. It is assembled by lots of small grains with voids and pores among them. It is also showed that small grain size is useful to enhance the sensitivity. At high temperatures, small grains tend to agglomerate into large entities, decreasing both surface areas and catalytic properties of the material. It is important to keep balance between decreasing grain sizes and stability.

References

[1]. M. Ghosh (2004). J. Nanosci. Nanotech. **4**. 136.

[2]. K. Koch (1985). Chem. Phys. Lett. **122**. 507.

[3]. M. D. Mustafa (2006). J. Mater. Chem. **16**. 2940.

[4]. J. Buha (2007). Crystal Growth & Design **7**. 113.

[5]. L. Guo, Y. L. Ji, H. Xu, P. Simon, Z. Wu (2002). J. Am. Chem. Soc. **124**. 14864.

[6]. C. Xu, G. Xu, Y. Liu and G. Wang (2000). Solid State Commun. **122**. 175.

[7]. S. Chakarbarti and G. Chaudhari (2004). Mater. Chem. Phys. **87**. 196.

[8]. R. C. Singh, O. Singh, M. P. Singh and P. S. Chandi (2008). Sensors & Actuators B. **135**. 352.

[9]. B. Liu and H. C. Zeng (2003). J. Am. Chem. Soc. **125**. 4430.

[10] . N. Verghese, L. S. Panchakarla, M. Hanapi, A. Govindaraj and C. N. R. Rao (2007). **42**. 2117.

[11]. L. S. Pahchakarla, A. Govindaraj and C. N. R. Rao (2007). J. Cluster Sci. **18**. 660.

[12]. K. R. Harikumar (1999). J. Phys. Chem. B. **103**. 2445.

[13]. O. Garcia-Martinez et al. (1997). Solid State Ionics **63**. 442.

[14]. S. S. Nath, D. Chakdar, G. Gope and D. K. Avasthi (2007). Nano Trends **3**. 1-10.

[15]. H. S. Virk and Poonam Sharma (2009). J. Nano Sci.