Gas sensors on zinc oxide nanostructures

Introduction

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, SnO_2, TiO_2, and WO_3.

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 (NO_2) 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.

In our work, we will develop a sensor for NO2 gas sensing based on our understanding in sensor mechanism and synthesis of ZnO nanorods, using simple hydrothermal methods. The various performance parameters of the sensor, namely gas selectivity, sensitivity, response and recovery time will be studied. The gas sensor test-bench developed in COEN (Centre of Excellence in Nanotechnology), AIT, will be employed for characterizing the sensor performance.

Chapter 2

Literature review

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

Metal oxide nanostructures

Metal oxides such as SnO_2, WO_3, TiO_2 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.

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.

The sign of response (resistance increase or decrease) leads to a simple classification: gases can be classified as oxidizing or reducing and oxides can also be classified as p or n type. P-type oxides show a resistance increase in the presence of traces of reducing gases and resistance decrease to oxidizing gases. n-type oxides show opposite behaviour. This behaviour also correlates with the effect of changing oxygen partial pressure (PO2).

Adsorption on surfaces

The sensing mechanism in metal oxide gas sensors is related to ionosorption of species over their surfaces. The most important ionosorbed species when operating in ambient air are oxygen, water, carbon and its compounds. High concentrations of carbon can block surface sites of adsorption on a metal oxide. In the temperature range between 100 °C and 500 °C, oxygen ionosorbs over metal oxide in molecular (O2-) or atomic form (O-). Hence the study of adsorption is of fundamental importance in the field of sensors.

Physisorption

In this weakest form of adsorption like van der waals forces, no true chemical bond between the surface and adsorbate (or reaction species) is established. This bonding is mainly due to the induced dipole moment of a nonpolar adsorbate interacting with its own image charges on the polarized surface. The bonding energy is rather weak in the order of 0. 1 eV.

Chemisorption

Chemisorption corresponds to the creation of chemical bonds between the adsorbate and surface and results in the electronic structure perturbation. In gas sensors, the target gas may be chemisorbed or physisorbed on the surface. When the gas species adsorb on the surface, molecules are either dissociated or diffused in the sensitive layer.

Based on the Temperature Programmed Desorption (TPD) and Electron Paramagnetic study (EPR) studies, at lower operating temperatures, oxygen is considered to be adsorbed in molecular form (either as neutral O2 (ads) or charged O2(ads) 2-) due to its lower activation energy. At higher temperatures it dissociates into atomic oxygen (either neutral O(ads) or singly ionized (charged) O(ads)- or doubly ionized O2(ads)-). Finally at very high temperatures the loss of lattice oxygen (first surface and then bulk) takes place. When a reducing gas like CO comes into contact with the surface.

These consume ionosorbed oxygen and in turn change the electrical conductance of metal oxide. The overall effect is a change of the density of ionosorbed oxygen that is detected as an increase of sensor conductance. Direct adsorption is also possible for the gaseous species like strongly electronegative NO2, which decreases the sensor conductance.

NO2 absorption on tin oxide surfaces was studied by temperature programmed desorption measurements and found that the adsorbates originating from NO2 are the same as those from NO, as NO2 molecule dissociates easily over the tin oxide surface. These adsorbates can be

divided into three types, two nitrosil types – (Sn – NO+ and Sn – NO-) and the nitrite type Sn – O-N= O. The nitrite type does not play any role in gas sensing since it is not involved in any electron exchange with the bulk of the semiconductor.

In practical applications, gas sensors are normally expected to operate in air, in the presence of humidity and interfering gases. In such cases, for operating temperatures in a range of 100 to 500 °C, at the surface of the sensitive material various oxygen, water and carbon dioxide related species are present. Some gas species form bonds by exchanging electrical charge with specific surface sites and others may form dipoles. Dipoles do not affect the concentration of free charge carriers and so they have no impact on the resistance of sensitive layer. Fig. 1 explains the simplified case of adsorbed oxygen ions and hydroxyl groups bound to an n-type metal oxide semiconductor. These adsorbed ions cause a band bending while the dipoles change the electron affinity when compared to the state before the adsorption . The changes of the work function (? F) are determined by band bending (qVs – due to ionosorption) and changes in the electron affinity (??) due to building of dipoles at the surface (M d+ – OH d-).

Ec, Ec, s – Energy level representing the bottom of the conduction band and at the surface respectively. Ev, Ev, s – Energy level representing the top of the valence band and at the surface respectively. Evac – vaccum level, EF – Fermi level, Φ – Work function, χ – Electron affinity.

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.

Static characteristics

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.

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.

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.

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.

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 measurand concentration as it did prior to being shut down.

Hysteresis

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

Response Time

The time taken by a sensor to arrive at a stable value is the response time. It is generally expressed as the time at which the output reaches a certain percentage (for instance 95%) of its final value, in response to a stepped change of the input. At the onset, the response time is very fast, followed by a long drawn tail before reaching steady state value, thus the response time are often expressed as 50% or 70% of the final time. Recovery time is defined as the time that the sensor takes to recover its resistance from exposed condition to the baseline value after target gas is cut out from the environment

Dynamic Range or Span

The range of input signals that will result in a meaningful output for the sensor is the dynamic range or span. All sensors are designed to perform over a specified range. Signals outside of this range may cause unacceptably large inaccuracies, and may even result in irreversible damage to the sensor.

Dynamic characteristics

The dynamic characteristics of a sensor represent the time response of the sensor system. The various important dynamic characteristics of sensors are discussed below,

Rise time

Rise time is defined as the time required by the sensor response to change from 10% to 90% of it final steady state value.

Settling time

It is the time taken by the sensor response to settle down to within a certain percentage of the steady state value.

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.

Improvement of selectivity by surface modifications

Mixing metal oxides with

1. Metals that function as catalysts
2. Binary compounds and multi-component materials
3. Doping

are 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.

The nature of noble metals, their oxidation state and their distribution on the surface are determining factors in gas sensor sensitivity and selectivity. To attain the homogenous distribution of noble metal on the surface is very difficult. Surface morphology has a significant effect on the shape and distribution of catalysts. Noble metal clusters have a tendency to accumulate at step edges and kinks of metal oxides during their deposition.

Catalysts based on noble metals can be poisoned by many organic and inorganic chemicals that contain sulphur (H2S, SO2, thiols) and phophorus. The excessive thickness of catalytic active additives can change their functions, turning into either shunting layer or active membrane filters, obstructing the penetration of detecting gas in the surface of gas sensing matrix. At certain conditions this quality can also be used for an improvement of gas sensors selectivity.

It has been studied that the incorporation of additional phases (different oxides) in nanocrystalline systems in small quantities can change the conditions of base oxide growth. SnO2 doped with Nb (0. 1 – 4 mol%) causes a decrease in crystallite size from 220 nm for pure SnO2 to about 30 nm for Nb (0. 1 mol%) doped samples. The additional influence observed due to doping is the change in film resistance. SnO2 doping by Nb and Sb in the range of 0. 01 and 1. 0 mol% during sol-gel preparation and annealed at 900 °C leads to film resistance decrease of 100 to 1000 times respectively, while doping with In resulted in a rise in film resistance by a factor of 100. The effect of doping on gas sensing properties of metal oxide gas sensors is different from the catalytic activity of these additives.

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.

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.

Synthesis of 1-D metal oxide nanostructures

Metal oxide nanostructures synthesis methods are broadly categorized as

1. Solution phase synthesis method, where the growth process is carried out in liquid. Since aqueous solutions are used, this process is otherwise termed as hydrothermal growth process.
2. Gas phase synthesis methoduses gaseous environment in closed chambers. The synthesis is carried out at high temperatures from 500 °C to 1500 °C.

Zinc oxide (ZnO)

ZnO is wide bandgap (Eg = 3. 4 eV) II – VI compound semiconductor which has a non-centrosymmetric wurtzite structure with polar surfaces and lattice parameters a = 0. 3296 and c = 0. 52065 nm. The structure of ZnO can be described as a number of alternating planes composed of tetrahedrally coordinated O2- and Zn2+ ions, stacked alternatively along the c-axis. The tetrahedral coordination in ZnO results in piezoelectric and pyroelectric properties. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (000-1)-O polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis.

Hydrothermal Synthesis of Zinc oxide nanostructures

Different techniques namely sol-gel, spray pyrolysis, hydrothermal method, electrospinning and thermal evaporation are prevalent for the synthesis of zinc oxide nanoparticles and nanorods. The hydrothermal process is an environmentally friendly process and does not require a complex vacuum environment. The hydrothermal process is surface independent and provides good control over the morphology of the nanostructures. ZnO nanorods growth on glass substrates by thermal decomposition of hexamethylenetetramine (HMT) and zinc nitrate is reported by Baruah et al. Thermal degradation of HMT releases hydroxyl ions which react with Zn2+ ions from ZnO. The role of HMT is to supply the hydroxyl ions to drive the precipitation reaction. Sugunan et al, have proposed that HMT being a long chain polymer and a nonpolar chelating agent, gets preferentially attached to the non polar facets of the zincitie crystal thereby cutting off the access of Zn2+ ions to them leaving only the polar (001) face for epitaxial growth.

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.

Tin oxide

Law et. al, analyzed room temperature sensing properties of a single crystalline tin oxide nanowire sensor towards nitrogen dioxide. NO2 chemisorb strongly on SnO2 surface and at room temperature desorption is not complete when the NO2 is removed. UV light was used to activate both the adsorption and desorption process. In the dark, oxygen adsorbs on the surface capturing electrons from the semiconductor and creates a depletion layer. When exposed to UV, photo-generated holes migrate to the surface and recombine with electrons releasing oxygen ions, with an increase in conductance. The detection limit was 2 – 10 ppm of nitrogen dioxide.

Kolmakov et. al studied the effect of catalysis in tin oxide single wire FET structures. The sensing capabilities of SnO2 single nano-wires and nanobelts in a FET configuration before and after functionalization with Pd catalyst was analysed. The improvement in the sensing performance after catalysation was reported to be the combined effect of spill-over of atomic oxygen formed catalytically on Pd clusters and migrating on SnO2 surface and also to the back spill-over effect in which weakly bound molecular oxygen migrates to Pd clusters and are catalytically dissociated.

Indium oxide

Indium oxide nanowires have been tested towards ethanol by Xiangfeng et. al. A mixture of In2O3 nanowire and polyvinyl alcohol solution was coated on alumina tubes with two gold contacts at the end; a heating wire was inserted in the tube to operate in the temperature range 100 – 500°C. The resistance

of the nanowires was monitored in presence of air, ethanol and other gases. The highest response was obtained with ethanol, the detection limit was estimated to be equal to 100 ppm.

Molybdenum oxide

Molybdenum oxide nanorods based gas sensing was reported. The MoO3 nanorods were characterized by high response to ethanol and CO at temperatures in the range of 100 °C. The response of thin films with the same structure was comparatively studied and nanorods based sensor resulted in one order of magnitude more sensitive due to the high surface to volume ratio and reduced lateral dimensions of the nanorods.

Other metal oxides

Sawicka et. al. presented the nitrogen sensing properties of tungsten oxide nanowires prepared with electrospinning. The effect of processing parameter variations was studied and a comparison with thin films prepared by sol-gel was also presented. WO3 nanowires showed better NO2 sensing performances compared to sol-gel processed films due to increase in surface area of nanowires.

A large amount of literature is available on the gas sensing properties of carbon nanotubes. Only little attention is put in the studies of gas sensing properties of metal oxide based tubular structures. Varghese et. al. studied the hydrogen sensing properties of titania nano-tubes. The tests were performed in nitrogen atmosphere and 1% H2. The response time increased with temperature and the response time was 2-3 min.

NO2 gas sensors based on ZnO nanostructures

Liu et. al reported the NO2 gas sensing properties of vertically aligned ZnO nanorod arrays prepared by hydrothermal method with zinc acetate and hexamethylenetetramine. The seed layer was deposited by ultrasonic spary pyrolysis. The aqueous hydrothermal solution was prepared by mixing equimolar ratio of zinc acetate dehydrate and HMT. The hydrothermal growth was carried out in a Teflon-lined stainless container. The substrate was put in the solution with the seeded face down and the container was sealed and kept at 110°C for three hours. The nanorod sensor shows a higher sensitivity than the ZnO film based sensor prepared by ultrasonic spray pyrolysis. The enhanced sensitivity is attributed to the higher aspect ratio of the nanorod structure and the sensitivity increases with the length of the nanorod. The relative response of the sensor is linearly proportional to NO2 concentration in the 0. 2 – 5 ppm range.

The NO2 gas sensing properties of semiconducting type gas sensors with channels composed of non-agglomerated, necked ZnO nanoparticles were investigated by Jun et. al. The heat treatment of the nanoparticles at 400°C led to their necking and coarsening. The slight necking of the nanoparticles with their neighbors also enhanced the conductivity of the channels, due to the lowering of the potential barrier. The response of the necked nanoparticle based sensor was reported to be as high as 100 when exposed to 0. 2 ppm of NO2 at 200 °C.

NO2 gas sensor based on ZnO nanorods grown by ultrasonic irradiation was reported to very high sensitivity with a very low detection limit of 10 ppb at 250°C. Sonochemical route was employed for the fabrication of vertically

aligned nanorods on a Pt electrode patterned alumina substrate. The total time requir