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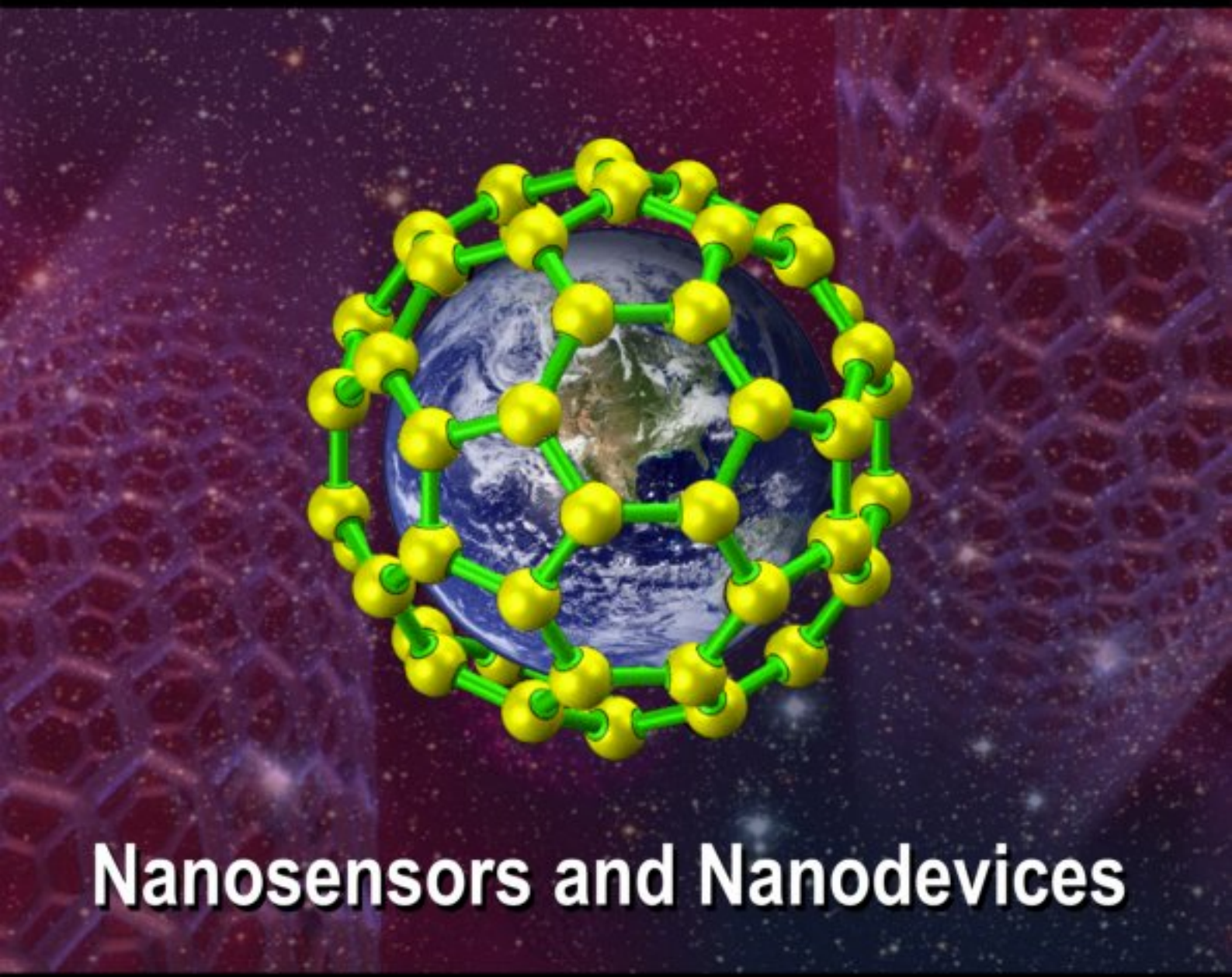

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Nanomaterials and Chemical Sensors

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Abstract: Nanomaterials and nanosensors are two most important iconic words of the modern science & Technology. Though nano technology is relatively a new area of research & development it will soon be included in the most modern electronic circuitry used for advanced computing systems. Since it will provide the potential link between the nanotechnology and the macroscopic world the development is primarily directed towards exploitation of nanotechnology to computer chip miniaturization and vast storage capacity. However, for implementation in the consumer products the present high cost of production must be overcome. There are different ways to make nanosensors e.g. top-down lithography, bottom-up assembly, and self molecular assembly. Consequently, nanomaterials & nanosensors have to be made compatible with the consumer technologies. The progress in detecting and sensing different chemical species with increased accuracy may transform the human society from uncertainty and inaccuracy to more precise and definite world of information. For example, extremely low concentrations of air pollutants or toxic materials in air & water around us can be accurately and economically detected in no time to save the human beings from the serious illnesses. Also, the medical sensors will help in diagnoses of the diseases, their treatment and in predicting the future profile of the individual so that the health insurance companies may exploit the opportunity to grant or to deny the health coverage. Other social issues like privacy invasion and security may be best monitored by the widespread use of the surveillance devices using nanosensors.

Keywords: Nanomaterials, Properties, Chemical & electrochemical sensors, Miniaturization, Applications.

1. Nanomaterials

Nanoscale materials are made of clusters of atoms and molecules. For example 3.5 atoms of gold or 8 atoms of hydrogen linked up in a row are nanometer long; a glucose molecule is about 1 nm size. Size of nanomaterials is intermediate between isolated atoms or molecules and bulk materials. At this scale the material shows exceptional properties. Use of quantum mechanics is required to explain the behavior of nanomaterials. Quantum effects and salient physical properties relevant at the nanoscale dimension are presented as follows [1-7].

(a) Properties of Nanomaterials

The mass of nanomaterials is extremely small and so the gravitational forces are negligible. As a result the electromagnetic forces are dominant in determining the behavior of nanomaterials. Also the wavelike nature has a more pronounced effect due to extremely small mass and their position is represented by wave (probability) function.

(i) Quantum Tunneling

According to quantum physics a particle with energy less than that required to jump the barrier has a finite probability of being found on the other side of the barrier. So it can be imagined that the particle passes into virtual tunnel through the barrier. We know that the thickness of the barrier must be comparable to the wavelength of the particle for tunneling effect and it is observed at nanometer level.

(ii) Quantum Confinement

In case of the nanomaterials like metals or semiconductors electrons are confined in space rather than free to move in the bulk. For semiconductors the band gap becomes large as compared to the bulk ones since the electrons exist in the discrete energy level. In very small dimensions the metals may behave like semiconductors due to the quantization of the energy levels and the disappearance of the band overlap normally present in metals.

(iii) Random Molecular Motion

Molecules move due to their kinetic energy (assuming that the sample is above absolute zero) and it is called random molecular motion. This motion is present in every material and it is very small compared to the size of the object. Thus it cannot influence on how the object moves. But at the nanoscale, this motion can be of the same extent as the size of the particles and can influence on how the molecules move.

(iv) Surface and Reactivity

Nanomaterials have the distinguished properties of increased surface to volume ratio compared to the bulk materials. The atoms and molecules at the surface or at an interface are different from those that exist in the interior of a material. When the crystal size decreases it exposes more and more surface. So fraction of atoms in the grain boundary increases. It is known that the grain boundaries contain a large density of defects states like vacancies and dangling bonds that play an important role in the transport properties of electrons of materials in general and of nanomaterials in particular. In fact, the grain

boundaries are nothing but metastable states and they have natural tendency to reduce their energy either by exchange or by sharing of electrons with other atoms. Therefore, the surface reactivity (or chemical reactivity) increases. Since a large fraction of atoms in nanomaterials is at the surface it influences some physical properties like melting point. For the same material, for example, the melting point is lower if it is nanosized. This happens because the surface atoms can be more easily removed than bulk atoms in the crystalline structure and so the total energy needed to overcome the intermolecular forces that hold the atoms is less in nanomaterials, resulting in the reduction of the melting point.

(v) Mechanical Properties

Some nanomaterials such as carbon nanotubes have inherent exceptional mechanical properties. These are extremely small tubes with honeycomb structure of graphite. Carbon nanotubes are hundred times stronger but six times lighter than steel. Therefore, the nanomaterials can also have improved mechanical properties than existing materials like metal, polymer, composites etc.

(b) Nanomaterials Used for Chemical Sensors

In recent times nanomaterials have become extremely popular for chemical & bio sensing, due to their interesting electrical conductivity, unique structural and catalytic properties, high loading, good stability and excellent penetrability. Carbon nanotube (CNT) (discussed later) can be used as electrode materials with useful properties for various potential applications including miniature biological devices. The electrochemical sensing using CNTs has been extensively studied and reviewed by different authors. The sensors showed higher response with lower work potential and minimum interference. Soluble carbon nanofibers have been reported to be used to modify glucose sensors that perform the electro reduction of dissolved oxygen at a low operating potential.

TiO_2, ZnO, and CuO nanotube arrays have been proved as promising functional materials for applications in chemical gas sensors and bio chemical sensors. Pt and Au nanoparticles with about 20 nm diameter and uniformly distributed in the nanotube channels can work as oxide- reaction centres to catalyse the oxidation of H_2O_2. Also the nanotubular TiO_2 can be used for the direct immobilization of glucose oxidase with a stable catalytic activity.

In recent years, researchers have explored the production of novel nano-scale metal oxides, noble metal-doped metal oxides, metal oxide-CNT nanocomposites, and metal oxide-polymer composites. Devices based on nanostructured metal oxides are cost-effective, highly sensitive due to the large surface-to-volume ratio of the Nanostructures, and show considerable selectivity to bio molecules. ZnO nanomaterial has been studied extensively in optics, optoelectronics, solar cells, sensors, and actuators owing to their semiconducting, optical and favourable electric properties in addition to the piezoelectric and pyroelectric properties [8-12]. Like its applications for gas sensors ZnO is attractive for the fabrication of the metal-oxide based biochemical sensors, due to its good biocompatibility, chemical stability, non-toxicity, electrochemical activity and fast electron transfer rate. However, sometimes the nanostructured ZnO shows poor mechanical stability, because the ZnO nano-structure is removed from the electrode surface during functionalization. Indeed, improved stability without loss of sensitivity or selectivity is one of the big challenges for glucose monitoring with these biosensors. Wang et al [13] prepared ZnO nanoparticles and coated them onto a multiwall carbon nanotube (MWNT)-modified electrode to improve the stability. Transition metal oxides significantly enhance direct oxidation of glucose compared with other metals that attribute to the catalytic effect resulting from the multi-electron oxidation mediated by surface metal oxide layers. Transition metals such as Cu and Ni can oxidize carbohydrate easily without surface poisoning. Unlike Cu and Ni, corresponding

oxides or hydroxides are relatively stable in air and solutions [14-15]. Natural abundance of copper oxide, its low production cost, good electrochemical and catalytic properties make the copper oxide to be one of the best materials for electrical, optical and photovoltaic devices, heterogeneous catalysis, magnetic storage media, gas sensing, field-emission emitters, lithium ion electrode etc. [16-18]. Recently the catalytic effect of copper oxide in relation to nonenzymetic glucose oxidation, voltammetric sensing of carbohydrates and hydrogen peroxide detection with ultra-sensitive response and good stability has been improved due to advances in nanoscience and nanotechnology [19]. The CuO nanowire can greatly promote electron transfer rate of glucose oxidation by increasing the electro catalytic active area. Moreover, the CuO modified electrodes can be used repeatedly without being contaminated by glucose oxidation by-product. Experimental data for the glucose detection are in good agreement with the results from the spectrophotometer method performed with real samples. TiO_2 nanomaterials are biocompatible and environmental friendly. Moreover, nanostructured TiO_2 provides better environment for enzyme immobilization by enlarging the surface area [20-21].

For glucose detection the attractive catalytic properties of transition metal oxides like CuO and NiO are interesting for nonenzymetic direct electro oxidation of glucose. A glucose biosensor was reported by Xie et al. [22] in which glucose oxidase was embedded inside TiO_2 nanotube channels where pyrrole was electropolymerized. Using pure Titania nanotube array the direct detection of hydrogen peroxide by electro catalytic reduction reaction was achieved with a detection limit down to 2.0×10^{-4} mmol/L. The glucose biosensor based on the glucose oxidase-titania/titanium electrode showed an excellent performance with a response time below 5.6 s and a detection limit of 2.0×10^{-3} mmol/L. The corresponding detection sensitivity was 45.5 μA L $mmol^{-1}$ cm^{-2}. The high response and low detection limit of this novel biosensor could be quite suitable for potential applications.

The nano-sized Au particles show extraordinary catalytic activity as revealed by recent studies. The Au nanopillars showed high electro catalytic activity not only in the reduction of hydrogen peroxide and molecular oxygen but also in the oxidation of glucose due to its nano-sized pillar array structure. An Au nano-structured film with active Au adatom was proposed. Good sensitivity of Pt-nanotube and macro porous Pt-modified electrodes to glucose has been shown. Sensors were fabricated by Pt nanoparticles immobilized on CNTs. Polypyrrole embedded with Pt nanoclusters provides a porous, biocompatible and highly catalytic platform. Other metal nanomaterial applied in fabrication of glucose sensors is copper (Cu) that showed good selectivity and sensitivity. Also Iridium, could detect H_2O_2 released from the enzymatic reactions with a favorable signal-to-noise ratio [23-27]. The silica nanoparticles and the non-doped nanocrystalline diamond have been reported for the same purpose. There is a report on an amperometric sensor based on polypyrrole nanotube array deposited on a Pt plated nano-porous alumina template as the electrode for an efficient enzyme loading and an increased surface area for sensing. Another nanoelectrode sensor like polypyrrole nanofibers with entrapped graphene oxide (GO) was recently fabricated [28-31] and was demonstrated for good biocatalytic activity to glucose.

An Au nano wire (NW) [32] array electrode was reported to be successfully fabricated by template-assisted deposition and transfer of nanowires onto a rigid glass substrate applied for nonenzymetic glucose sensor. It was observed by electrochemical investigation that the partial oxidation of glucose on Au NW array electrode takes place at more negative potential than that on the Au film electrode. Also, the kinetics of partial oxidation of glucose on Au - NW array revealed that three different electrochemical reactions for the voltammetric detection of glucose could be used with the peak currents linear on the wide range of glucose concentrations. The amperometric detection within physiologically important range of glucose concentrations was possible with a very high sensitivity of 309.0 AmM^{-1} cm^{-2}.

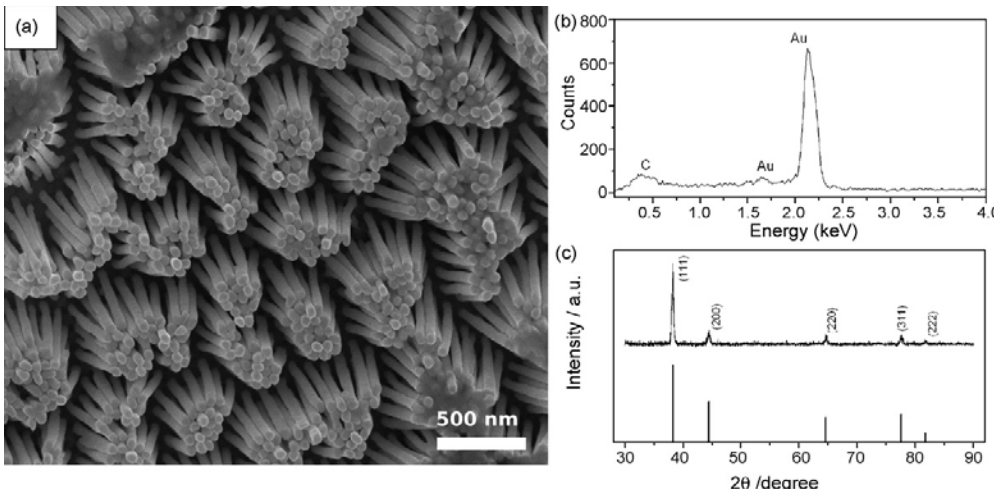


Fig. 1. FESEM of gold nano wire.
(Reprinted from Sensors and Actuators, B, 142, S. Cherevko, C-H. Chung ,"Gold nanowire array electrode for non-enzymatic voltammetric and amperometric glucose detection", pp 216, Copyright 2009, with permission from Elsevier)

The advantage of using a NW array electrode is that the roughness of such electrodes is smaller than the so called chronoamperometric diffusion field and therefore the faraday current of rapidly oxidizable or reducible chemicals is proportional to the apparent geometric area of the electrode and independent of its roughness. On the other hand, the faraday current for kinetically controlled electrochemical reactions is sensitive to the nanoscopic features of the electrode and, proportional to its entire area. Nanostructures such as nanowires, nanoparticles and CNTs have been used as smart building blocks for emerging electronic and sensing devices. Metallic nanowires allow higher sensitivity, higher capture efficiency and faster response time because of their large adsorption surface (large surface to volume ratio), high electrical conductivity and small diffusion time. Au nanowires promote better electron transfer between the enzymes and the electrodes [9].

Surface modified multiwall CNTs with a biocompatible polymer like polyvinyl alcohol was reported to convert the hydrophobic nanotubes surface into a hydrophilic one that facilitates efficient attachment of biomolecules. CNTs modification can improve the response of lactate electrode sensors. Pt nanoparticles were electrodeposited onto a multiwall CNTs film by a multi-potential step technique and precasted on a glassy carbon or boron-doped diamond electrode. This technique significantly improved the conductivity, stability and electro activity for detection of lactate and other biomolecules.

2. Chemical Sensors

Chemical sensor is a self contained probe that provides the real time information about the chemical composition of its surroundings. It has to perform two functions:

- A specific interaction with a component of the analyte sample known as Recognition or Sensing.
- A physical or a chemical property can be converted into a measurable physical signal (electrical, optical, etc.) and is known as Transduction. The signal can be used for measuring the analyte concentration through appropriate calibration procedure. As for an example, the glass electrode can recognize the hydrogen ion and measure its concentration by a selective ion exchange process using the development of a membrane electric potential in presence of hydrogen ions.

2.1. Advantages of Chemical Sensors

- The dedicated sensors can substitute the standard analytical procedures and can help in fast detection and analysis.
- The chemical quantities can be automatically monitored.
- The portable sensor instruments can be conveniently used for field analysis.

2.2. Applications

- Process analytical procedures can be efficiently adopted in industry.
- Monitoring of the chemical pollutions in the environment can be automatically performed.
- Fast and/or *in situ* monitoring of drugs and biologically important compounds such as O_2, CO_2 and glucose content in blood are possible in biomedical science.
- Automatic control of important chemical parameters, such as pH, O_2 and CO_2 content, or nutrient concentrations can be carried out in food industry and Biotechnology

Chemical sensors have a chemical or molecular target to be measured and so the biosensors can be considered as a subset of chemical sensors because of the similar transduction methods as those for chemical sensors. Chemical sensor arrays with instrumentation, like the electronic nose or electronic tongue are known to address chemically complex analyte like taste, odour, toxicity, or freshness. Therefore the definition of a chemical sensor may be ‘‘a small device that as the result of a chemical interaction or process between the analyte gas and the sensor device, transforms chemical or biochemical information of a quantitative or qualitative type into an analytically useful signal.’’[33]. The wide use of chemical sensors includes applications for critical care, safety, industrial hygiene, process controls, product quality controls, human comfort controls, automotive emissions monitoring, clinical diagnostics, home safety alarms, and homeland security (Table 1) [34]. Both economic and social benefits of chemical sensors are possible through these applications.

Table 1. Application of Chemical sensors.

Application	Detected Chemicals and Gases
Automotive	O_2, H_2 , CO, NO*x* , HCs,
Water treatment	pH, Cl_2, CO_2 , O_2, O_3, H_2S,
Food	Bactreria, biologicals, chemicals, fungal toxins, humidity, pH, CO_2
Agriculture	NH_3 , amines, humidity, CO_2 , pesticides, herbicides
Military	Agents, explosives, propellants
IAQ	CO, CH_4 , humidity, CO_2 , VOCs
Industrial safety	Indoor air quality, toxic gases, combustible gases, O_2
Petrochemical	HCX, and conventional pollutants
Steel	O_2, H_2 , CO, conventional pollutants
Medical	O_2 , glucose, urea, CO_2 , pH, Na_1, K_1, Ca, Cl_2, bio-molecules, H2S,Infectious disease, ketones, anesthesia gases
Environmental	SO*x* , CO_2 , NO*x* , HCs , NH_3 , H_2S, pH, heavy metal ions
Utilities [gas, electric]	O_2 , CO, HCs, NO*x* , SO*x* , CO_2

The chemical sensors can be classified into two categories e.g. direct and indirect sensors.

(a) Direct Sensor

A measured electrical output by a chemical reaction or the presence of a chemical can be directly correlated to the quantity, e.g. the capacitive moisture sensor where the capacitance is directly proportional to the amount of water present between the two plates of the capacitor.

(b) Indirect Sensor

It works on the indirect reading of the sensed stimulus e.g. optical smoke detector where a photo resistor is illuminated by a source and smoke is allowed to flow and alter the light intensity, its velocity, its phase or some other measurable property.

There are also other chemical sensors, which are more complex due to the involvement of more transduction steps. In this review paper we have classified the chemical sensors into two types, e.g. (I) Gas sensors and (II) Electrochemical sensors.

(I) Gas Sensors

(i) Metal Oxide Based Solid-state Resistive Gas Sensor

The cost of establishing and implementing ordinary monitoring systems is extremely high; use of analytical instruments are time-consuming, expensive, and can seldom be applied for real-time monitoring in the field, even though they can provide a precise analysis. Hence the need for low cost, fast responsive and highly sensitive solid-state chemical sensors to detect air pollutant has increased in this century. The wide band gap semiconducting oxides (ZnO, TiO_2, SnO_2 etc) are suitable materials for the fabrication of inexpensive gas sensitive structure because of their versatile material properties and robust nature and low cost of production [35-37].

Semiconducting oxides are the fundamentals of smart devices as both the structure and morphology of these materials can be tailored precisely and accordingly, they are referred as functional oxides. They have two structural characteristics: cations with mixed valence states and anions with deficiencies. By varying either one or both of these characteristics, the electrical, optical, magnetic, and chemical properties can be tuned, giving the possibility of fabricating smart devices. The structures of functional oxides are very diverse and varied, and there are endless new phenomena and applications. Such unique characteristics make oxides one of the most diverse classes of materials, with properties covering almost all aspects of materials science and physics, in areas like semiconductors, superconductivity, Ferro electricity, and magnetism.

Since the demonstration almost 50 years ago that the adsorption of gas on the surface of a semiconductor can bring about a significant change in the electrical resistance of the material, there has been a sustained and successful effort to make use of this change for the purposes of gas detection [38-39]. Detection of toxic and flammable (H_2, CH_4, NOx, SOx, COx, H_2S etc) gases is a subject of growing importance in both domestic and industrial environments. Metal oxides such as Ga_2O_3, SnO_2, WO_3, TiO_2, and ZnO [37, 40-44] are stable physically and chemically and are widely investigated for gas and humidity detection. Sensing performances, especially sensitivity, are controlled by three independent factors: the receptor function, transducer function, and utility. Receptor function concerns the ability of the oxide surface to interact with the target gas. Chemical properties of the surface oxygen of the oxide itself are responsible for this interaction in an oxide device, but this function can be largely modified. A considerable change in the sensitivity takes place when an additive (noble

metal, acidic or basic oxide) is loaded on the oxide surface**.** Transducer function concerns the ability to convert the signal caused by chemical interaction of the oxide surface (work function change) into electrical signal. This function can be realized by the measure of the current through a system containing an innumerable number of grains and grain boundaries, to which a double-Schottky barrier model can be applied.

It has been observed by almost all researchers working with oxide semiconductors for gas sensing that the operation of such sensors with selectivity for a particular gas is extremely difficult, specially when the change in the electrical properties are used as the sensor signal. Use of sensor arrays and artificial neural network can normally solve this problem. In fact, today's chemical sensors are much more reliable with the implementation of ANN logic to improve the selectivity [45].

(ii) Principle of Gas Sensing

It is well known that the performance of gas sensors can be improved by incorporation of noble metals on the oxide surface. SnO_2 based gas sensors in the form of thick film, porous pellets or thin films and with Pt or Pd modifications are widely applied for monitoring explosive and toxic gases in industry, urban and domestic life [46]. Such promoting effects are undoubtedly related to the catalytic activities of the noble metals for the oxidation of hydrocarbons. In case of planar type resistive gas sensors two metal contacts are taken from the metal oxide. A polycrystalline semiconductor has a structure with a large number of grains and grain boundaries. In contrast to the single crystalline materials, polycrystalline materials give rise to local potential barriers, which arise between the grains. The electric properties of the surface of the thin film and the surface boundaries of the grains are affected by the adsorption and desorption of gaseous molecules. Oxygen ions can be found at the material boundaries. At elevated temperature O_2 is chemisorbed by gaining one further electron from the surface Due to this chemisorption the resistivity of the material increases.

$$O + e^- \longleftrightarrow O^- [150\ ^oC - 300\ ^o C] \quad (1)$$

$$2O + e^- \longleftrightarrow O_2^- [30^oC - 150\ ^oC] \quad (2)$$

Reducing Gas:

Reducing gases like methane & hydrogen react with chemisorbed oxygen at the material boundaries. A negative charge carrier (electron) is added to the bulk and hence the resistance decreases.

$$CH_4 + 4O^-_{(ads)} \longrightarrow CO_{2\,(air)} + 2H_2O + 2e^-_{(bulk)} \quad (3)$$

$$H_2 + O^- \longrightarrow H_2O + 2e^-_{(bulk)}$$

Oxidizing gas:

Oxidized gases like NOx; COx etc react with chemisorbed oxygen at the material boundaries. A negative charge carrier (electron) is taken from the bulk and hence the resistance increases.

$$NO_2 + O^- \longrightarrow NO + 2O^- \quad (4)$$

By measuring the change in the conductivity of the semiconductor oxide thin films we can detect the reducing gases [47-48].

For p-type semiconductor the effect is just the opposite of n-type semiconductor because for p-type semiconductor the majority carrier is hole and adsorption of O^- on the semiconductor increases the hole conductivity and hence by reaction with reducing gases the hole conductivity decreases. In case of the oxidizing gases, the reaction with chemisorbed oxygen increases the hole conductivity further by electrons from the surface of the semiconductors.

A. Grain Size Effect

Nano crystalline feature is a single phase or multiphase of reduced size (1 nm to 100nm) with at least of one dimension. When the crystal size is decreasing, more and more surface is exposed. So fraction of atoms at the grain boundary increases and the grain boundaries contain a large density of defects like vacancies and dangling bonds that can play an important role in the transport properties of electrons in nano materials. As the grain boundaries are metastable states they want to reduce their energy either by exchange of electrons or by sharing electrons with other atoms thereby increasing surface reactivity (or chemical reactivity). Xu et. al [36] proposed a model to explain the dependence of crystal size on the depletion layer due to adsorption of oxygen, to explain the high sensitivity of nanocrystalline metal oxide gas sensors. Later, A. Rothschild et. al [49] showed that the conductivity increases linearly with decreasing trapped charge states, and that the sensitivity to the gas-induced variations in the trapped charge density is proportional to $1/D$, where D is the average grain size. Fig. 2 shows a schematic of few grains of nanocrystalline metal oxide thin films and the space charge region around the surface of each grain at the intergrain contacts. The space charge region, being depleted of electrons, is more resistive than the bulk. When the sensor is exposed to reducing gases, the electrons trapped by the oxygen return to the oxide grains, leading to a decrease in the potential barrier height and thus a decrease in the resistance. The crystallites in the gas sensing elements are connected to the neighboring crystallites either by grain boundary or by necks. When the grain size (D) is greater than the depletion layer (L) width ($D>>2L$) most of the volume of the crystallites is unaffected by the surface interactions with the gas phase. In this case the conductivity between two grains is due to the grain boundary contacts. In case of $D> 2L$, the grain size decrease in the depletion region extends deeper into the grains due to adsorption of oxygen causing a decrease in the conductivity. The conductivity depends not only on the grain boundary but also on the cross sectional area of the channels (neck control). When $D<2L$.the depletion region extends throughout the whole grains and the crystallites are almost fully depleted of electrons. As a result the conductivity decreases through the junction and so the change of conductivity is very large in presence of reducing gases, yielding a high gas response. Fig. 2 demonstrates the three situations schematically. Further, nanocrystalline metal oxides can reduce the operating temperature of the gas sensors. H. Zhang and co-workers [50] reported that the surface or interfacial tension decreases with decreasing particle size because of the increase in the potential energy of the bulk atoms of the particles. Smaller particles with increased molar free energy are prone to adsorption per unit area of molecules or ions onto their surfaces in order to decrease the total free energy and to become more stable, and therefore, the smaller particles have higher adsorption coefficient for gases. Thus, the adsorption of oxidizing or reducing gases takes place relatively easily onto the nanocrystalline metal oxide surfaces.

B. Gas sensing behavior of Nanocrystalline Metal Oxides

Basu et al [51-52] prepared electrochemically grown ZnO-nanodot based methane and hydrogen sensors for low temperature applications. The FESEM of the grown ZnO is shown in Fig. 3(a). The sample was also Pd modified for better functional characterization of the sensors. The crystal size as determined from XRD was below 10nm. . For the planar structures both contacts were taken from the Pd-Ag (26 %) electrodes on the ZnO surface and the separation between two electrodes was 3 mm.

The electrical connections from the sensor device were made by using fine copper wires and silver paste. The schematic of the planar structures is shown in Fig. 3(b).

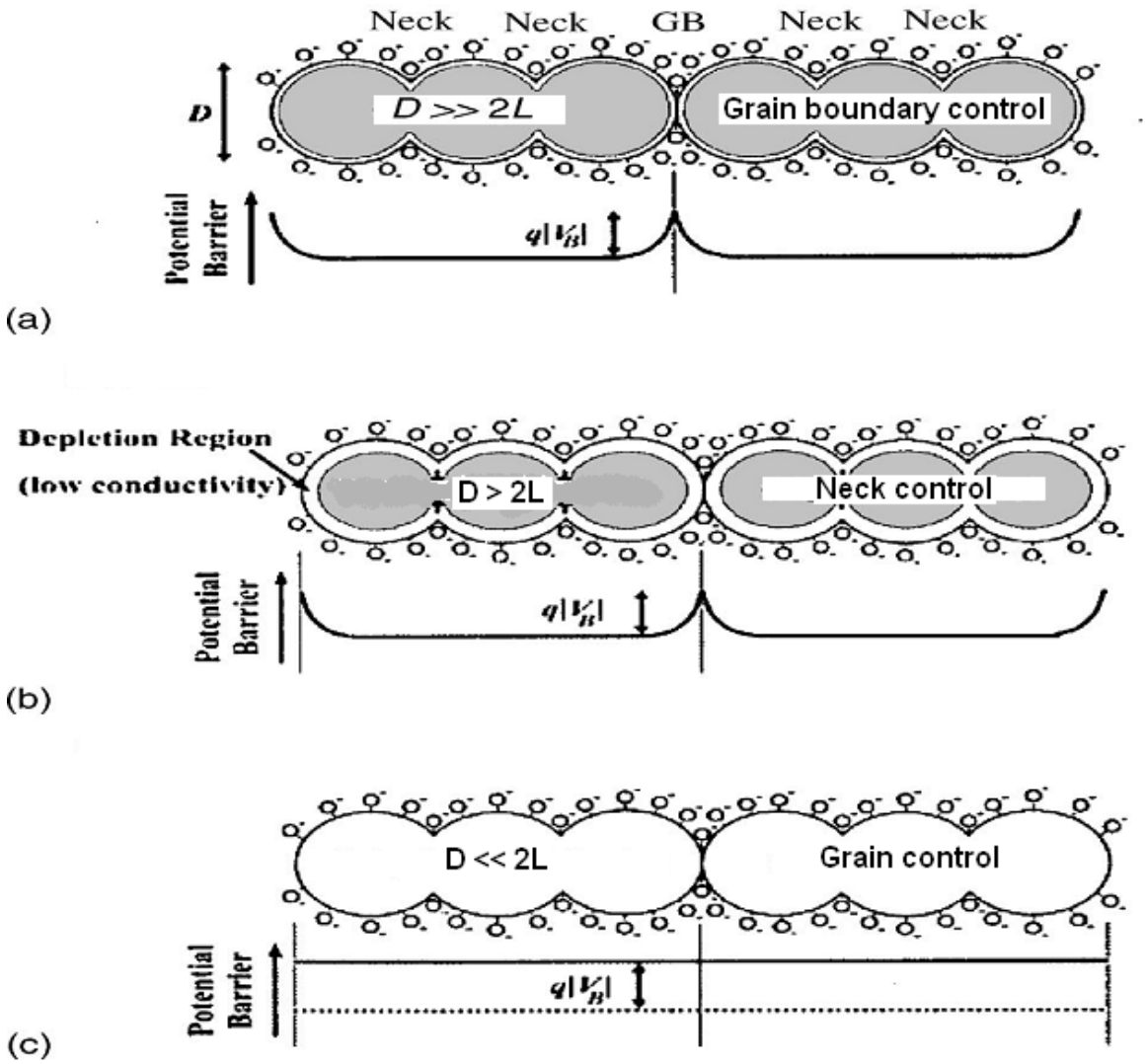


Fig. 2. Schematic of few grains of nanocrystalline ZnO thin films and the space charge region around the surface of each grain at the inter grain contacts.
(Reprinted with permission from "The effect of grain size on the sensitivity of nanocrystalline metal-oxide gas sensors", Journal of Applied Physics, 95 (2004) 6374 by A. Rothschild, Y. Komen ,Copyright 2004: American Institute of Physics).

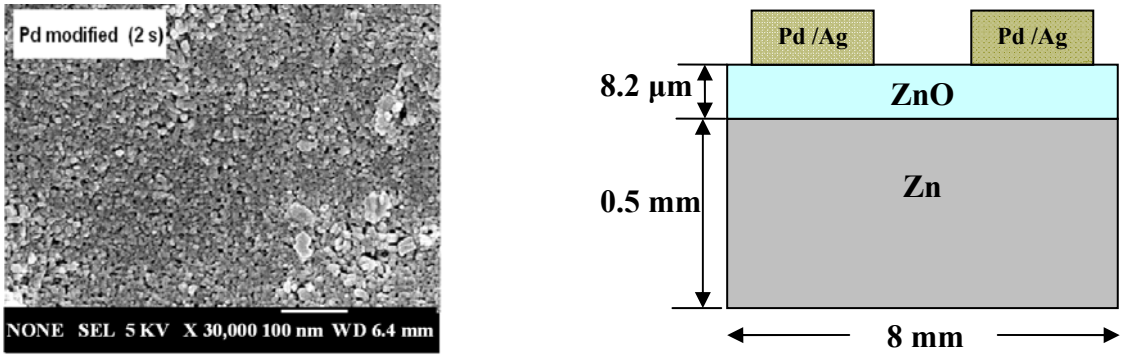
The Pd loaded nanocrystalline (below 10 nm) ZnO enhances the oxygen spillover process [51-56] resulting in a large amount of chemisorbed oxygen that yields a high electrostatic potential across the Pd-Ag/ZnO Schottky interface. Subsequently methane or hydrogen reacts with this adsorbed oxygen and produces H_2O as shown in the equation 6 and 7 respectively.

$$CH_4 + 2O_2^- \longleftrightarrow CO_2 + 2H_2O + e^- \quad (6)$$

$$H_2 + 2O_2^- \longleftrightarrow H_2O + e^- \quad (7)$$

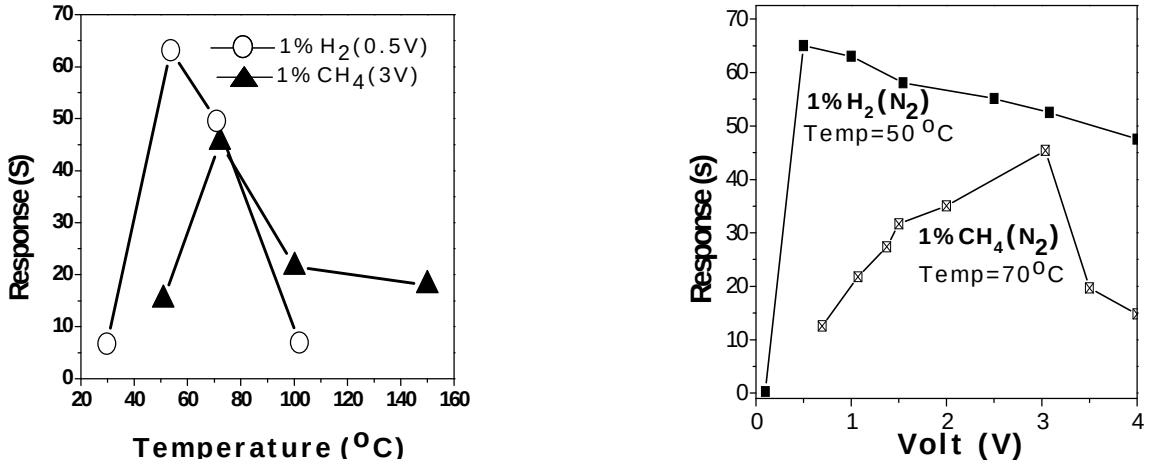
The electrons on the surface of ZnO enhance the current through the electrodes. I-V characteristics of the planar sensor structures were studied with 1% methane and 1% hydrogen using pure nitrogen as the carrier gas over the temperature range 30ºC - 100ºC in separate experiments. The variations of the

response with operating temperature and with biasing voltage have been plotted for planar sensor structures and are shown in Fig. 4.



(a) (b)

Fig. 3. (a) FESEM pictures of Pd modified ZnO thin films and (b) schematic of planar configuration for gas sensing.
(Reprinted from Sensors and Actuators, B, 135, P. K. Basu, S. K. Jana, H. Sasha and S. Basu, "Low Temperature Methane Sensing by Electrochemically Grown and Surface Modified ZnO Thin films", 81, Copyright 2008: with permission from Elsevier).



(a) (b)

Fig. 4. (a) Response vs. temperature and (b) response vs. voltage curves of the planar sensor in 1% methane and 1 % hydrogen using nitrogen as carrier gas.
(Reprinted from Sensors and Actuators, B, 135, P. K. Basu, S. K. Jana, H. Sasha and S. Basu, "Low Temperature Methane Sensing by Electrochemically Grown and Surface Modified ZnO Thin films", 81, Copyright 2008: with permission from Elsevier).

It is evident from the figures 4 (a) & (b) that the maximum response for methane at 3V bias is obtained at 70º C, the lowest temperature so far reported while hydrogen shows maximum response at 50º C and 0.5V. For nanocrystalline structure the adsorption activation energy is normally low and it is further reduced due to presence of dispersed Pd acting as a catalyst over ZnO surface [57]. The transient response of the planar sensor in different gas concentrations (0.01 %, 0.05 %, 0.1 %, 0.5 % and 1 %) and with nitrogen and synthetic air as carrier gases respectively, in separate experiments, are shown in Fig. 5.

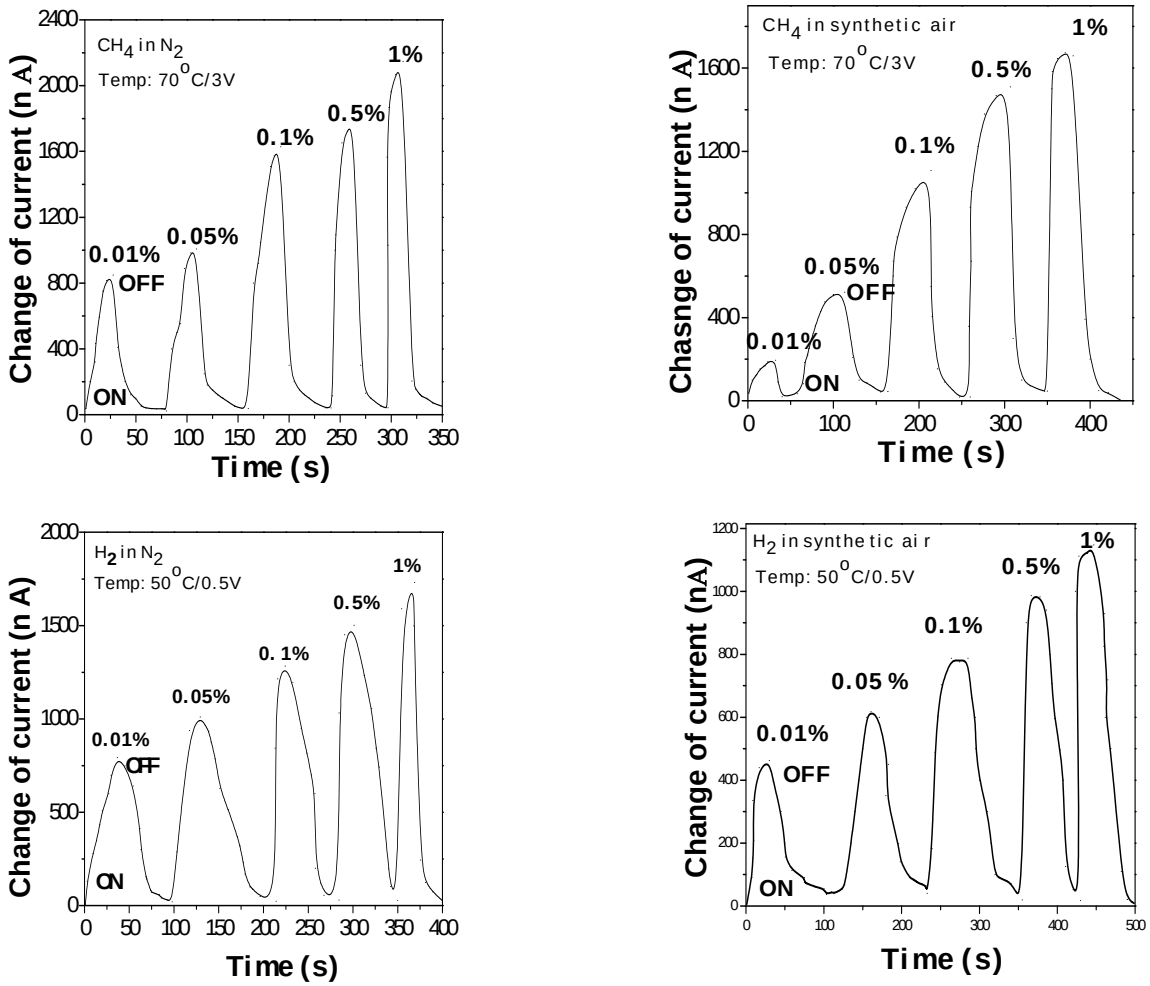


Fig. 5. Transient response curves of the planar structure for methane and hydrogen using nitrogen and synthetic air as carrier gases. For methane the sensor was operated at 70 °C and at 3V bias while hydrogen was operated at 50 °C and at 0.5 V bias.

(Reprinted from Sensors and Actuators, B, 135, P. K. Basu, S. K. Jana, H. Saha and S. Basu, "Low Temperature Methane Sensing by Electrochemically Grown and Surface Modified ZnO Thin films", 81, Copyright 2008: with permission from Elsevier)

The response time and the recovery time as derived from the transient response curves are summarized in Table 2 and Table 3.

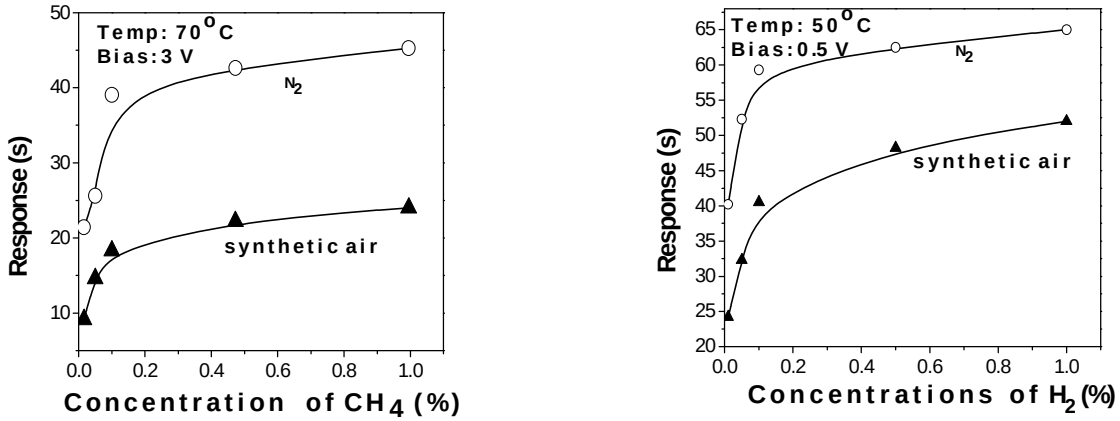
Table 2. The results of the planar sensor in different concentrations of methane and hydrogen at 70 °C and 50 °C respectively using nitrogen as a carrier gas.

% of Gas	Response time (s)		Recovery time (s)		Response	
	methane	hydrogen	methane	hydrogen	methane	hydrogen
0.01	16.1	12.8	22.6	42.3	34.5	29.3
0.05	12.9	11.8	26.3	53.1	28.9	27.9
0.1	10.9	9.9	40.2	60.2	27.7	24.8
0.5	8.8	6.8	43.1	63.5	24.7	23.6
1	4.8	3.2	48.4	65.0	22.4	21.4

Table 3. The results of the planar sensor in different concentrations of methane and hydrogen at 70 ^{o}C and 50 ^{o}C respectively using synthetic air as a carrier gas.

% of Gas	Response time (s)		Recovery time (s)		Response	
	methane	hydrogen	methane	hydrogen	methane	hydrogen
0.01	19.2	22.3	9.2	24.2	34.2	46.2
0.05	17.4	16.4	14.6	32.3	32.8	44.4
0.1	16.4	8.2	18.3	40.5	29.6	34.2
0.5	15.2	5.3	21.6	48.2	27.4	29.6
1	12.6	4.2	25.7	52.0	23.4	26.8

From Fig. 6 it is observed that response of hydrogen gets saturated at 1000 ppm and above, most probably due to the fact that the active surface area of the sensor is already occupied. So, further increase of target gas concentration does not change the response of the sensors. This is supported by the observation of K. Christmann et al [57], which clearly states that with increasing coverage (θ) the sticking coefficient initially goes down sharply and then tends towards saturation with lower slope.



(a) (b)

Fig. 6. Concentrations vs. response curves of the planar sensor for (a) methane and (b) hydrogen using nitrogen and synthetic air as carrier gases.

From Tables 2 and 3 it is found that the response time is shorter than the recovery time. When gas supply is cut off and air is allowed to flow into the sensing chamber, oxygen is adsorbed on crystalline ZnO by spillover technique as mentioned earlier and the out diffusion of adsorbed hydrogen from the junction takes place simultaneously. The chemisorbed oxygen reacts with hydrogen and produces H_2O. As a result, electrons of the chemisorbed oxygen come back to the ZnO surface and the current through the electrodes increases instead of decreasing. This process continues until all the atomic hydrogen desorbs from the junction and reacts with oxygen causing the recovery time relatively longer than the response time. It is evident from Fig. 5 that initially the current increases in presence of target gases and then gets saturated. After withdrawing the gas flow the current decreases with a slope less sharp than that after the gas is on. From the adsorption-desorption kinetics it can be explained that desorption always takes place at higher temperature than adsorption. Some of hydrogen atoms obtained through dissociative chemisorptions of methane or hydrogen molecules remain adsorbed on nanoporous ZnO, and as a result the current flow kinetics gets sluggish causing the electrode current taking longer time to come back to its original base line value. By increasing the temperature or by

supplying more oxygen the complete recovery might be possible with faster kinetics and thus faster recovery time could be achieved.

Nanotube-based sensors include metal oxides such as Co_3O_4, Fe_2O_3, SnO_2, and TiO_2 and metal tubes like Pt and Pd that have also great potential for sensing. Li et al. [58] reported that Co_3O_4 nanotubes exhibit superior gas sensing properties for H_2. It was suggested that the change of resistance is caused by the adsorption and desorption of gas molecules on the sensing surface consisting of the inside hollow structure and the porous texture of the nanotubes that provide more active sites in the three dimensional configuration. This enables access of more detecting gases. Fe_2O_3 shows high response to H_2 and C_2H_5OH at room temperature [59]. Recently, Liu and Liu [60] reported a single square shaped SnO_2 nanotube ethanol sensor provided with to two interdigitated Pt electrodes. The advantages were shown to be dramatically accelerated transport of gas/liquid in and out of the box beams, significantly increased active surface areas, increased flexibility in surface modification for chemically or biologically selective catalysis, drastically enhanced transport of ionic and electronic defects in the solid state (perpendicular to the wall thickness) due to shorter diffusion lengths, increased population of defects at the surfaces/ interfaces for fast electrode kinetics and quantum interactions at the nanoscale.

Nanowire based gas sensors are also very popular now a days [61]. Such structures have high aspect ratio (i.e. size confinement in two coordinates) & better crystallinity. They consume less power and yield higher integration densities. Due to large surface-to-volume ratio and Debye length (the distance over which a local electric field affects the distribution of free charge carriers) comparable to the size, they exhibit superior gas response at room temperature in comparison to their bulk and thin film counterparts. The applied gate potential of the nanowire configured field-effect transistors (FETs), can effectively control surface processes. Moreover, the carrier diffusion time at the surface is significantly reduced, resulting to a faster response and recovery. Some researchers have investigated devices based on zinc oxide (ZnO) nanowires configured as FETs (Fig. 7) to build high performance sensors [61-62].

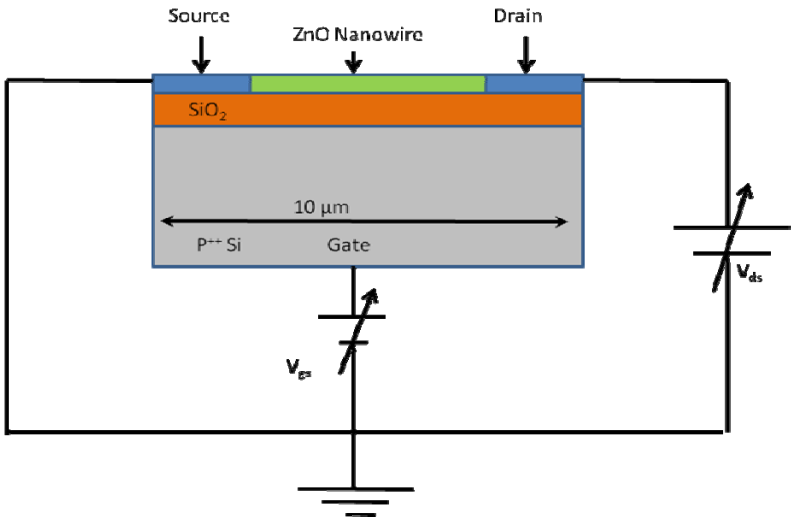


Fig. 7. Schematic of nanowire based FET structure.

Single crystalline ZnO nanowires (with a typical diameter of about 50 nm) were synthesized via a chemical vapor deposition method. Electrical measurements showed the ZnO nanowires to be *n*-type with the measured room-temperature electron concentration of the order 10^{19} cm^{-3}, and the electron mobility ranging from 20 to 100 cm^2/Vs. The charge transfer between the semiconductor and the chemical species adsorbed on the oxygen-vacancy sites is the origin of the sensing mechanism of the

metal oxide and the relative change of conductance on exposure to a target gas determines the sensitivity. For example, the conductance of ZnO nanowires decreases with the introduction of NO_2 and at room temperature more than 50 % conductance change was observed on exposure to 0.6 ppm NO_2. To compare, doped ZnO thin films achieved less than 2% conductance change when exposed to 1.5 ppm NO_2. This demonstrates a high potential of nanowire sensors with superior sensitivity.

The sensitivity can also be tuned by a transverse electric field induced by the gate of the FET configuration. Above a threshold gate voltage (the voltage at which the electrons are depleted in the channel), the sensitivity decreases with the increasing gate voltage. So the gate voltage can be used as a knob to adjust the sensitivity range. More significantly, the gate potential can be electrically tuned to desorb the gas molecules, thereby adjusting the recovery time to the desired scale.

Since the available thermal energy is usually lower than the activation energy for desorptions, chemical sensing is generally not reversible at room temperature and this also causes a long recovery time. Ultraviolet (UV) illumination may be a common method for refreshing a sensor but this increases the complexity of the sensor design, and the recovery time still may be fairly long. A gate-induced refreshing mechanism may be much superior and convenient. It is known that the conductance of a nanowire based gas sensor can be electrically recovered by applying a negative gate voltage with a value much larger than the threshold voltage. This reduces the chemisorptions rate, and the hole migration to the surface (driven by the negative field) leads to a discharge of chemisorbed species thereby reverting the channel conductance and refreshing the sensor efficiently at room temperature without including any additional hardware to the devices. However, in spite of the enhanced sensitivity and faster recovery time, the nanowire sensors face the challenge of selectivity.

As already mentioned above, the enhanced response of the Q1D (Quasi One-Dimension) systems to the chemical environment is due to large surface-to-volume ratio that is related to the aspect ratio of the Q1D systems. So it is obvious that the radius of the nanowires significantly affects their chemical sensitivity. The dependence of sensitivity to O_2 on the radius of the ZnO nanowire was experimentally studied and is plotted in Fig. 8. In fact, this dependence can also be derived from the Drude model. Z. Fan and J. G. Liu [63] calculated the relation of conductance, G of nanowire with radius r and length l and it was expressed as:

$$G = \frac{\pi r^2}{l} n_e \mu_e$$

where n_e and μ_e are the electron concentration and the electron mobility respectively.

$$n_e = n_0 \exp\frac{2\alpha N_s}{r}$$

where n_0 is the electron concentration before the exposure of nanowires to O_2, Ns and α represent the surface density of chemisorbed O_2 molecules and the charge transfer coefficient respectively. Therefore, upon chemisorptions of the sensing gas the relation becomes,

$$\frac{\Delta G}{G_0} = \frac{2}{r}\frac{\alpha N_s}{n_a}$$

The above equation apparently corroborates the plot shown in Fig. 8 and it clearly demonstrates that the smaller the diameter of nanowires the more effective is the chemisorptions on the nanowire surface and thus the more sensitivity for gases

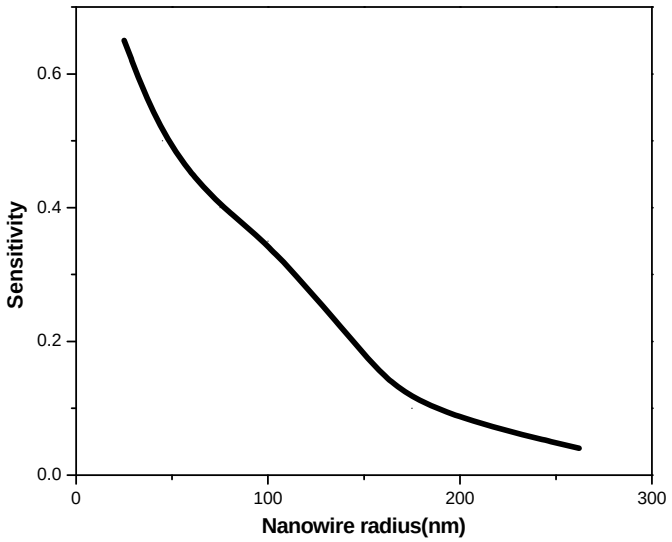


Fig. 8. Nanowire radius dependent sensitivity to O_2.

Metal nanowires and nanotubes have also shown great interest for sensing H_2 or hydrogen containing molecules and the hydrogen sensing by palladium nanowires has been experimentally studied in recent times [63–65]. The increase in resistivity in presence of hydrogen due to conversion of palladium to palladium hydride was reported earlier and therefore Pd alloys were used for H_2 sensing [76-69]. But recently, different sensing mechanisms were proposed depending on the properties of nanoscale materials [70–81]. The study of the hydrogen-induced percolation in discontinuous films or between nanoclusters and break junction formation in electrodeposited Pd mesowires [63, 82-83] was focused. The relatively big width of the breaks (25–35 nm) and relatively small active area of the mesowires limit hydrogen sensing below 1 %. The decrease of resistivity under hydrogen gas exposure was observed in these types of sensors and was believed to be due to percolation effect. On the other hand, both percolation and break junction formation mechanisms were assumed for a pulse-like hydrogen sensing response in Pd nanoparticle layers [84-86]. The scientists have investigated the influence of these two mechanisms on electrical resistivity of nanowires and nanotube arrays. The adsorption and diffusion of hydrogen atoms into palladium lead to an increase in resistivity due to electron scattering. On the other hand, the Pd lattice expansion because of the formation of PdH*x* phase induces a slight increase in the nanowire diameter and thus the increase of overall conductivity. However, when hydrogen is taken off, the inverse process takes place. In that case, the superposition of these two mechanisms creates difficulty in explaining the use of such an array as an active component in a hydrogen sensor. However, the high conductivity of continuous Pd film deposited on backside of anodic aluminium oxide (AAO) diminishes the effect of conductivity increment due to improvement of the connections between the nanowires. In fact, the sensor response of hydrogen at concentrations below 2.5 % was very small and was not very stable. The same logical arguments may be used for hydrogen sensing by nanotube array.

Pd nanotube has also a great potential to sense H_2 or hydrogen like molecules. The change of nanotube morphology on hydrogen exposure is schematically demonstrated in Fig. 9. Before activation the conductivity of the as deposited nanotube array is poor due to a poor contact between the nanotubes [84]. The diffusion of H_2 enlarges the diameter of the nanotubes and improves the contact. As a result the nanotube array conductivity increases.

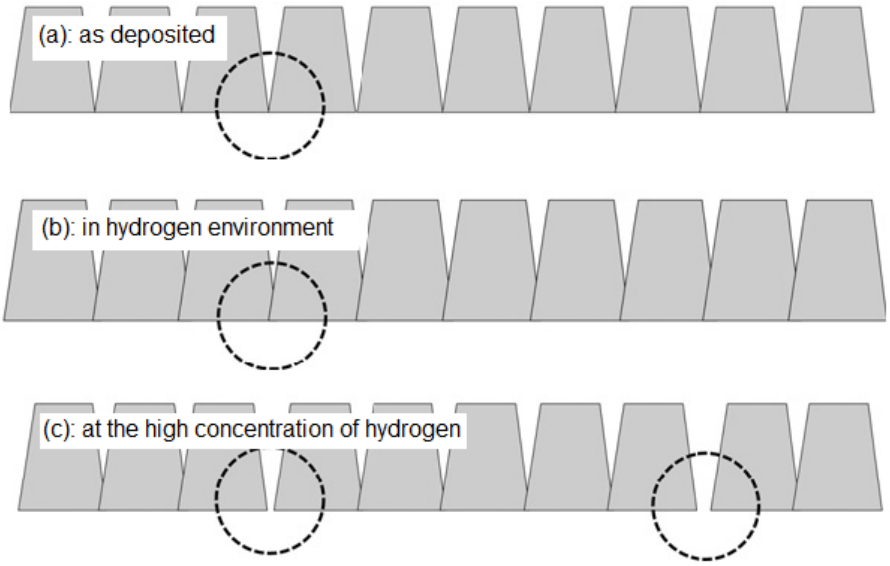


Fig. 9. Schematic representation of nanotube array sensor operation. (a) Continuous array of as-deposited conical Pd nanotube; (b) improvement in contact between nanotube under H_2 was exposed; (c) the array with nanocracks formed after strain induced by 1–2.5% H_2 released.
(Reprinted from Sensors and Actuators, B, 136, S. Cherevko, N. Kulyk, J. Fu, C-H. Chung "Hydrogen sensing performance of electrodeposited conidial palladium nanowire and nanotube arrays", 388, Copyright 2009: with permission from Elsevier).

This mechanism is valid until the applied hydrogen concentration is below the limit of inducing the phase transformation of Pd from alpha(Pd-α) to beta(Pd-β) form during "activation". Once the concentration is large enough for the phase transition, the reverse process generates & accumulates strain leading to the formation of the cracks as a result of tensile stress release. When H_2 is exposed to the sensor again, these nanocracks come closer and the conductivity drastically rises. The stable response to the tens of loading/unloading cycles proves again that such mechanism is valid for lower hydrogen concentrations.

(II) Electrochemical Sensors

Bio molecular analyses in a chemistry laboratory are expensive and time-consuming. One of the main challenges today is the development of methods to perform the rapid '*in situ*' analyses. These methods must be sensitive, accurate, and be able to determine various substances with different properties in 'real-life' samples. Due to their high sensitivity and selectivity, portable size, rapid response and low-cost, electrochemical sensors are ideally suited for the measurement of biomolecules as analyte of interest. The applications of nanomaterials as electrochemical sensor for biochemical detection are discussed here [85-87].

A. Principle

"Electrochemistry implies the transfer of charge from an electrode to another phase, which can be a solid or a liquid sample. During this process chemical changes take place at the electrodes and the charge is conducted through the bulk of the sample phase. Both the electrode reactions and/or the charge transport can be modulated chemically and serve as the basis of the sensing [88]."

Electrochemical sensors may be classified on the basis of potentiometric, amperometric, or conductivity measurements. For each type of measurement with the electrochemical cell a specific design is required and the structure of electrochemical sensors is shown in Fig. 10.

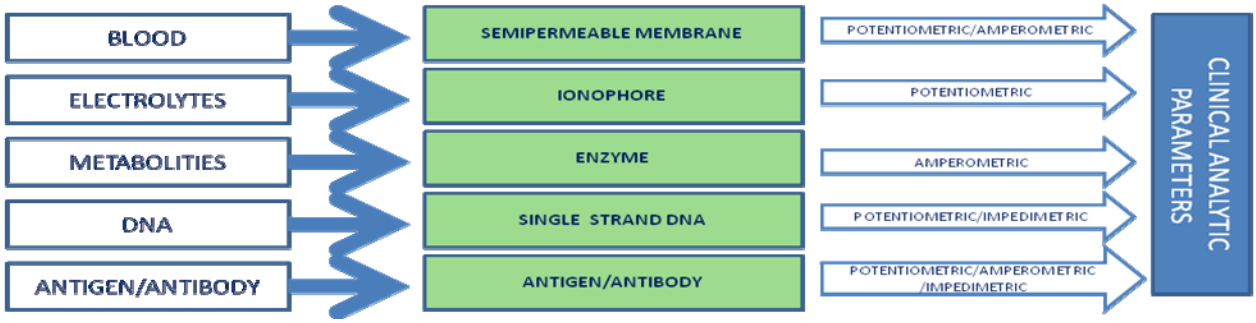


Fig. 10. Procedures for clinical analysis using electrochemical sensors. [85].

(a) Potentiometric Sensors

In potentiometric sensors, a very small current is allowed to measure the potential difference between the reference electrode and the indicator electrode without polarizing the electrochemical cell. The reference electrode is meant for providing a constant half-cell potential while the indicator electrode exhibits a variable potential depending upon the concentration of a specific analyte in a solution. The potential change is related to the logarithm of concentration. The relation between the potential difference at the interface and the activities (concentrations) of species *i* in sample phases (*s*) and in the electrode phase (β) is given by the Nernst equation:

$$E = E_0 + \frac{RT}{Z_i F} \ln \frac{a_i^s}{a_i^\beta},$$

where E_0 is the standard electrode potential of the sensor electrode; a_i is the activity of the ion, R is the universal gas constant; T is the absolute temperature; F is the Faraday constant and Z_i is the valency of the ion. The ion-selective electrode (ISE) is a potentiometric sensor for the measurements in the electrolyte phases. Mostly, a potentiometric sensor comprises a membrane (either a solid like glass and inorganic crystal or a plasticized polymer) with a unique composition and the ISE composition is chosen to indicate a potential that is primarily associated with the ion of interest via a selective binding process at the membrane-electrolyte interface [85-86].

Fig. 11 (a) shows the cell configuration of a conventional liquid junction ISE. In this type of potentiometric sensor a reversible ion or electron transport mechanism prevails at the ion-selective electrode. On the other hand, in solid contact electrode sensor illustrated in Fig. 11(b) polymer membrane is deposited directly onto the solid electrode and there is no liquid electrolyte solution internally.

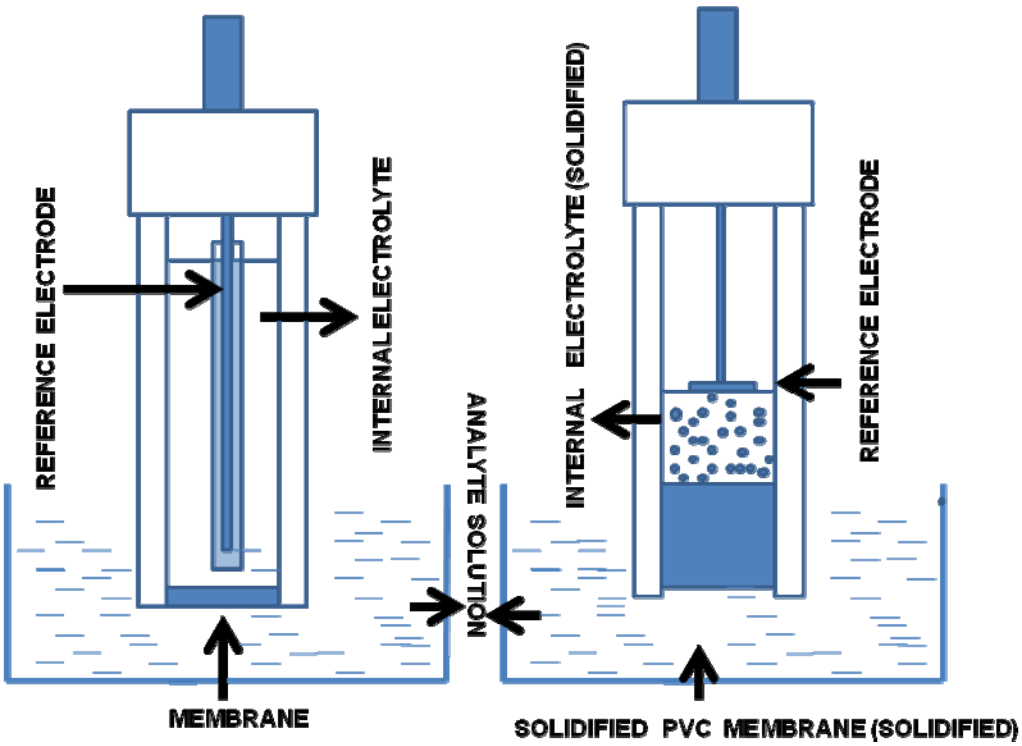


Fig. 11. The schematic of: (a) liquid junction ISE and (b) solid-contact ISE (redrawn from [85]).

(b) Amperometric Sensors

Amperometry is a method of electrochemical analysis in which the signal of interest is current and it is linearly dependent upon the concentration of the analyte. As the chemical species are oxidized or reduced (redox reactions) on inert metal electrodes, electrons are transferred from the analyte to the working electrode or vice versa [85-86]. The electron flow direction depends upon the properties of the analyte and it can be controlled by the potential applied to the working electrode. Two or three electrodes may be present in an amperometric cell. Usually the working electrode is a noble metal like platinum (Pt) or gold (Au) and the potential applied to the working electrode is measured and controlled by a reference electrode, usually Ag/AgCl that provides a fixed potential. Sometimes a third electrode, known as the counter or the auxiliary electrode is also used. By amperometric measurement a linear current vs. ion-concentration characteristics can be obtained using diffusion-controlled processes in the "limiting current operating mode". The measured cell current i.e. the diffusion current determines the analyte concentration quantitatively. Based on the amperometric measurements there are three "generations" of biosensors due to the different electron transfer processes. First-generation biosensors cause the electrical response because of the diffusion of normal product of the reaction to the transducer and the second-generation biosensors involve specific "mediators" between the reaction and the transducer for the improved response. In the third generation biosensors the reaction itself causes the response without the direct involvement of any product or mediator diffusion.

(c) Conductometric Sensors

Conductometric sensors measure the electrolyte conductivity that varies when the cell is exposed to different environments. The sensing effect is due to the change of the number of mobile charge carriers in the electrolyte. The electrolyte shows ohmic behavior with the non-polarized electrodes in the AC supply mode operations during conductometric measurements. Since the conductivity is a linear function of the ion concentration in the electrolyte the method can be used for sensor applications.

However, it is nonspecific for a given type of ion and so it functions as a non-selective sensor. The most essential conditions for using this sensor are the absence of polarization and limiting current operation mode. Thus, small amplitude alternating bias is used for the measurements with frequencies where the capacitive coupling is still not determining the impedance measurement.

B. Applications of Electrochemical Sensors

(i) Glucose Detection

The proper absorption of glucose in the body is biologically important, and the lack of it can create diabetes with the risk for renal failure, retinal and neural complications. So for diagnosis of diabetes the detection of glucose in blood is medically important.

Principle of Electrochemical Reactions:

The electrochemical reactions proceed as follows to detect GOx (glucose oxidase):

$$\text{D-glucose} + O_2 + H_2O \longrightarrow \text{D- gluconic acid} + H_2O_2$$

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$

By adding glucose dehydrogenase (GDH) the electrochemical reactions using electron transfer mediator in the glucose sensors proceed as follows:

$$GDH_{(OX)} + \text{D-glucose} \longrightarrow GDH_{(red)} + \sigma\text{-glucolactone}$$

$$\text{Mediator}_{(OX)} + GDH_{(red)} \longrightarrow \text{Mediator}_{(red)} + GDH_{(OX)}$$

$$\text{Mediator}_{(red)} \longrightarrow \text{Mediator}_{(OX)} + e^-$$

Sol-gel precursor mixture of 3-glycidoxypropyltrimethoxysilane with methyltrimethoxysilane or tetraethoxysilane and ionic liquid methylimidazolium hexafluophosphate provides a unique microenvironment for the immobilization of GOx. GOx adsorbed in hexagonal mesoporous silica retains its bioactivity and stability [85-89]. LB (Langmuir Blodget) film was employed for GOx immobilization because very thin film in nanoscale might produce a highly sensitive sensor with ultra fast response time. Conducting polymers have been receiving great and broad interests in clinical diagnosis of blood sugar [90-96]. There are many advantages of conducting polymers for preparing sensors like efficient transfer of electric charge and considerable flexibility of chemical structure. Researchers also indicated doping of redox enzyme within polypyrrole.

(ii) pH Detection

A preliminary test with surface charge field effect silicon nanowire device as a chemical sensor was performed by detection of pH level of the solution. [92, 97]. Fig. 12 shows the detection result of pH level by the silicon nanowire sensor of 100 nm width and 6 μm lengths.

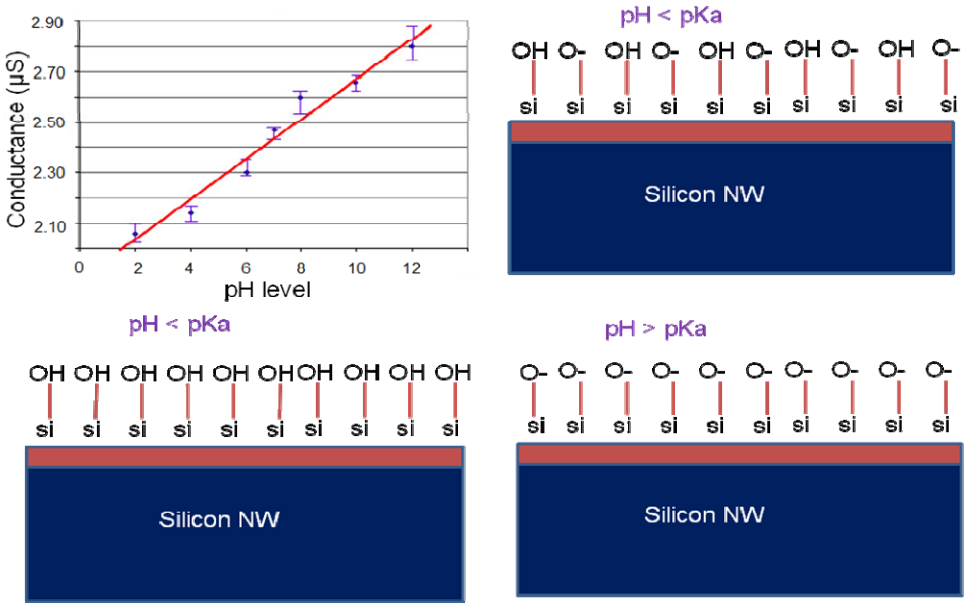


Fig. 12. pH level detection of solution by silicon nanowire sensor. The Change of electrical conductance with solutions of different pH level (approximately) and the proposed mechanism are displayed here. (Reprinted from Biosensors and Bioelectronics, 22, I. Park, Z. Li , X. Li, Albert P. Pisano , R. S. Williams "Towards the silicon nanowire-based sensor for intracellular biochemical detection", 2065, Copyright 2007: with permission from Elsevier).

At pH < p*K*a, the concentration of available proton ion (H+) is low and so the electrical conductance is low. On the other hand, when the pH > p*K*a, the electrical conductance becomes higher. This shows the usefulness of silicon nanowire chemical sensor based upon the concentration of surface charge around the silicon nanowire. More protonation on surface hydroxyl groups and accumulation of positive surface charge for pH < p*K*a, the boron doped p-type Si shows depletion of mobile charge carriers (holes) around the perimeter of the silicon nanowire. It can be stated qualitatively that less the pH value, the more protonation on the surface, and therefore the less conductance in the nanowire. If For pH above p*K*a, the surface hydroxyl groups follow the deprotonation process by generating negative ions on the nanowire surface. The mobile charge carrier depletion is reduced and more carriers are accumulated in the nanowire. Consequently, the electrical conductance of silicon nanowire is increased. The sensor shows an approximate linear relationship between pH level and electrical conductance of the nanowire with a sensitivity of about 79.4 nS/pH. From these experimental results, it has been verified that this silicon nanowire sensor works quite well as a chemical field effect sensor and can be used for the detection of charged protein molecules with the proper functionalization of the surface. Research is being currently pursued in this direction.

(iii) pO_2 Measurement

In this sensor configuration the dissolved oxygen molecules in solution reach the electrode surface and there occurs a redox reaction. In the typical Clark-type O_2 electrode, the function of the cathode-working electrode is to reduce oxygen as given by the half-cell reaction,

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

The half-cell reaction at the anode-counter electrode where the oxidation takes place and provides the return path to complete the circuit is given by [98]:

$$4Ag + 4Cl^- \rightarrow 4AgCl + 4e^-$$

The current output can be calibrated linearly with respect to the dissolved oxygen by applying a potentiostatic bias voltage of approximately 0.7 V.

(iv) pCO_2 Measurement

When dissolved CO_2 in solution diffuses into the internal electrolyte of the liquid junction potentiometric sensor, the following reactions occur:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$H_2CO_3 \longrightarrow {}_{H}{}^{+} + HCO_3^-$$

$$HCO_3^- \longrightarrow {}_{H}{}^{+} + CO_3^-$$

At the steady state chemical equilibrium, the concentration of CO_2 and H_2CO_3 are equal. The partial pressure is related to the pH of the sample because H_2CO_3 dissociates into H+ and HCO_3-. When the ionic buffer, such as sodium bicarbonate ($NaHCO_3$), is present, the pH is related to pCO_2 and the activity (concentration) of the sodium ion by,

$$\mathrm{pH} = -\lg \frac{K_1 \alpha p\mathrm{CO}_2}{\alpha_{\mathrm{Na}^+}}$$

Here K_1 is the dissociation constant and α is the solubility coefficient for CO_2. The pH change is directly related to pCO_2 because the sodium ion activity remains almost constant.

3. Carbon Nano Tube Chemical Sensors

Sensors continue to make significant impact in everyday life with applications ranging from biomedical to automotive industry. Intensive research activities are continuing throughout the world for developing new materials and technologies for sensing. This is further intensified with the advancement of nanotechnology in order to develop miniaturized sensors with reduced weight, lower power consumption, and low cost materials. Of late, the discovery of carbon nanotubes (CNTs) has brought keen interest among the researchers to develop CNT-based sensors for various applications in the medical diagnosis, food industry, environmental pollutions and chemical warfare.

Small size, high strength, high electrical and thermal conductivity, and high specific surface area have enabled CNT sensors to be noted as the next-generation sensors to revolutionize the sensor industry. CNTs are hexagonal networks of carbon atoms of approximately 1 nm diameter and 1 to 100 microns length. CNT is essentially a sheet of graphite rolled-up cylindrically. There are two types of nanotubes depending upon the arrangement of the graphene cylinders, e.g. single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) (Fig. 13). SWNTs have only one single layer of graphene cylinders; while MWNTs have many layers (approximately 50).Synthesized CNTs can be either aligned or random in nature. However, there are certain limitations of using CNTs for sensing in spite of their promising applications.

Based on the advantages of CNTs compared to other materials as mentioned above several papers have been published using CNTs as the sensing material in pressure, flow, thermal, gas, optical, mass, position, stress, strain, chemical, and biological sensors [98-99].

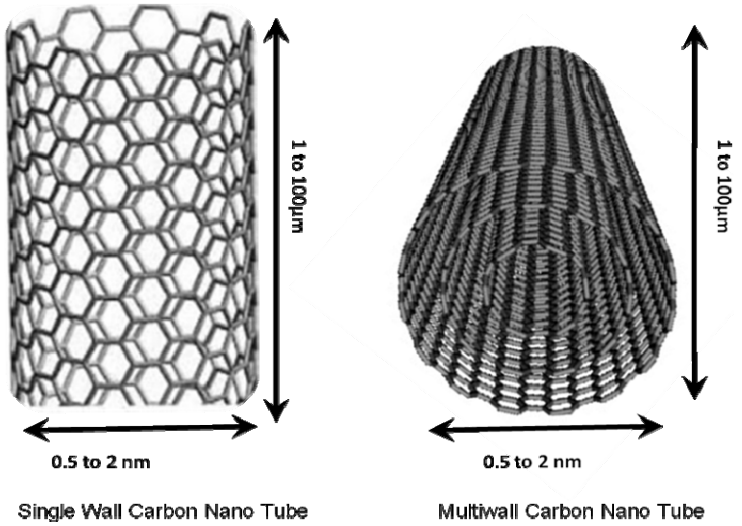


Fig. 13. A schematic of carbon nano tube with both single wall and multiwall configurations.

The implantable sensors may be very useful for health assessment and CNT based nanosensors are more appropriate for this purpose as they are thousands of times smaller than MEMS sensors and they consume much less power. Also, they are less sensitive to temperature variations that are necessary for reliable biomedical sensor performance. So, CNT-based nanosensors can be suitable as implantable sensors for continuous monitoring of pulse rate, temperature, blood glucose, and for diagnosing various diseases [100–102]. CNTs can also be potentially used for repairing the damaged cells or killing the tumors by chemical reactions. Implantable nanosensors can also monitor heart's activity level by regulating the heartbeats [103]. CNT based nano bio chemical sensors may also be used to detect DNA sequences in the body and DNA related to a particular disease may be detected. The use of CNT-based sensors can avoid problems of other implantable sensors with high current flowing that can cause inflammation, and can eliminate the need to draw and test blood samples. The devices can be administered through the skin and it is much less painful [104].

Sensors and bio chemical sensors are popular for widely use in food industry for quality control and for safety of food products as we know that the food contaminated by bacterial pathogens may lead to numerous diseases [105]. Efficient quality assurance is becoming increasingly important in the food industry. By the upsurge of nanotechnology and the unique properties of carbon nanotubes, CNT-based sensors show great potential for applications in the food industry including fish & meat freshness evaluation. After constant storage certain volatile components (such as, dimethyl and trimethyl amines, ethyl acetate etc) are released due to the initial bacterial putrification of fish & meat**,** By detecting the concentration of these chemicals, the quality control of fish & meat can be possible. Philip et al. [103] reported CNT/polymethylmethacrylate (PMMA) gas sensor for detecting different organic vapors including ethyl acetate. The use of a CNT-based gas sensor provides a non-destructive, noncontact method for food analysis, which is desirable and convenient for quality control in the food industry. CNT-based chemical sensors can also be used to detect undesired chemical residues and other environmental contaminants in animal drugs, food additives, herbicides, and pesticides in raw and processed foods. The promising aspect of CNT-based sensor research includes evaluation of the quality of fruits and vegetables. CNT-based gas sensors can offer improved performance for real-time monitoring of environmental pollution, combustible gas leak detection/alarms, chemical warfare agents (e.g., TNT or RDX and nerve agents such as GB or VX). CNT-based miniaturized gas sensors, in contrast to conventional solid-state gas sensors working at relatively high temperature, can be operated at room temperature. Moreover, gas sensors based on CNTs can be built in different geometrical features, not limited by the micro fabrication techniques and can offer reliable response [104-106]. The CNT sensors can ensure that the level of CO does remain within safe limit in the car

park regions and in the ventilation systems coupled with an exhaust fan. By monitoring different level of CO concentration by CNT based CO sensors, the fans in ventilation system can be automatically set for starting, stopping or operating with variable speed. Also CNT-based sensors can be installed to monitor NO_2 where significant diesel traffics are prevalent**.** CNT-based electrochemical biosensors are suitable for wastewater monitoring [107-109]. The results of wastewater real sample tests using CNT biosensors were found to be in good agreement with the results of other genotoxicity tests .Humidity and temperature conditions impact the quantity and quality of the product directly in the agriculture and fishing industry. CNT-based humidity sensors can be effectively applied to monitor the humidity in green house agriculture. MWNT-coated quartz crystal microbalance humidity sensor has been experimentally proved to monitor relative humidity over the range, 5–97% RH with a response and recovery time of about 60 and 70 seconds respectively. Plants cannot grow properly if the concentration of CO_2 is too high because the excess CO_2 get dissolved in water and produce carbonic acid that makes the soil more acidic. CNT -based CO_2 sensors can be used to monitor the concentration of CO_2 within the green house to maintain an optimal environment for the desirable growth of plants. An amperometric biosensor was developed by Sotiropoulou and Chaniotakis [108] using aligned MWNTs as the immobilization matrix and it was grown on platinum (Pt) substrate that served as the transduction platform for signal monitoring. The sensor arrays were treated with acid to remove the impurities like amorphous carbon that was included during the production process and with air to peel off the outer graphite layers from the nanotubes in separate experiments. The response and sensitivity of the acid treated sensor was found to be very high compared to the air-treated sensor after immobilization of the enzyme (e.g. glucose oxidase).

Kong et al [104] reported the change in electrical resistance of semiconducting SWNTs on exposure to gases like nitrogen dioxide (NO_2), ammonia (NH_3), and oxygen (O_2). The nanotube sensors exhibited the response time less than other sensors. Semiconducting SWNTs can function at room temperature with appreciably high sensitivity and this is an advantage of SWNTs-based chemical sensors.

However, Modi et al**.** [109] reported that the CNT gas sensors working on changes in electrical conductance have certain limitations, such as poor diffusion kinetics, inability to identify gases with low adsorption energies, and poor selectivity for gas mixtures. They also observed that the changes in moisture, temperature and gas-flow velocity affect the conductance of CNTs to large extent. They could overcome these limitations by proposing gas ionization sensors based on the electrical breakdown of a range of gases and gas mixtures at the tips of CNTs. Aluminium was used as cathode and the vertically aligned MWNT film (25–30 nm in diameter, 30 μm in length, and 50 nm separation between nanotubes) grown on SiO_2 substrate was used as anode. A glass insulator separated the electrodes. This ionization sensor showed good selectivity and sensitivity, and was not affected by the humidity, temperature, and gas-flow rates. Santhanam et al [110] used a nanocomposite of MWNTs and poly (3-methylthiophene) to develop a chemical sensor. Apart from this, nanocomposites of MWNTs and poly (3-methylthiophene) can be used to develop a chemical sensor. The sensor was sensitive to different chloromethane and changed its electrical resistance in presence of them. However, the response time of the sensor was found to be longer and was of the order 60 to 120 sec.

Of late Graphene based chemical sensors have got special attention of the researchers. Graphene is a single sheet or just a 2D structure of carbon in which the carbon atoms are SP^2 hybridized. They form a wide 2-dimensional hexagonal sheet in which each carbon is bonded to 3 other carbon atoms [111]. This sheet when rolled is called carbon Nanotube (Fig. 14). We can just imagine a sheet of paper rolled to form a tube like structure. These graphene sheets are arranged layer by layer in the graphite and these sheets are bonded to each other by weak van der waals forces but these are strong enough to make graphite hard. Graphene has emerged out to be a potential semiconductor and due to its abundance we can say that this can prove out to be a boon in semiconductor electronics [112]. Imagine a sheet of material that is just one atom thick, yet super-strong, highly conductive, practically transparent and able to reveal new secrets of fundamental physics.

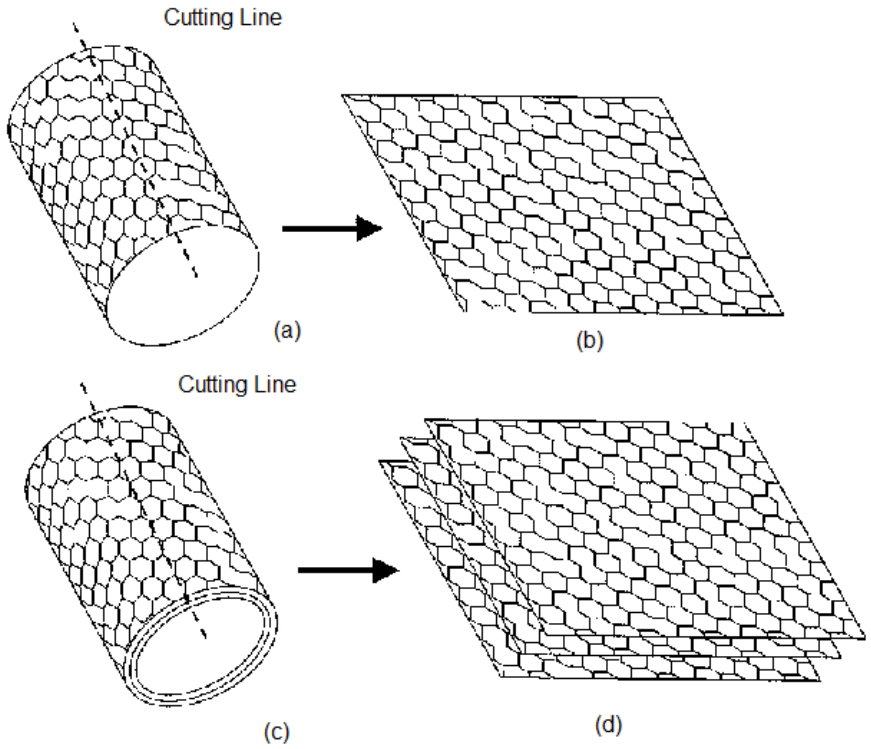


Fig. 14. Schematic of the (a) single wall carbon nano tube; (b) single layer grapheme; (c) multi wall carbon nano tube, and (d) multi layer graphene.

Graphene has few intrinsic charge carriers but remains conductive, as told by team member Andre Geim, of the University of Manchester and Nobel Laureate in Physics to Chemistry World. So when you add just a single electron it changes the resistivity significantly. Geim said that it should be possible to functionalise the surface of graphene to detect defined species. Graphene has the ultimate sensitivity because in principle it cannot be beaten - you cannot get more sensitive than a single molecule [113]. Hydrogen sensors from Pd-functionalized multi-layer graphene nanoribbon networks are fabricated. The fabrication method of these networks is simple, low cost, and scalable, and their high specific surface area facilitates efficient functionalization and gas adsorption. These networks show high sensitivity to hydrogen at parts-per-million concentration levels at room temperature with a fast response and recovery time. Graphene has been attracting great interest because of its distinctive band structure and physical properties. Today, graphene is limited to small sizes because it is produced mostly by exfoliating graphite. Large-area graphene films of the order of centimeters have been grown on copper substrates by chemical vapor deposition using methane. The films are predominantly single-layer graphene, with a small percentage (less than 5%) of the area having few layers, and are continuous across copper surface steps and grain boundaries. The low solubility of carbon in copper appears to help make this growth process self-limiting. Graphene film transfer processes to arbitrary substrates have been developed, and the dual-gate field-effect transistors fabricated on silicon/silicon dioxide substrates have shown electron mobility as high as 4050 square centimeters per volt per second at room temperature. The thermally reduced graphene oxide (GO) [114,115] shows p-type semiconducting behavior in ambient conditions and are responsive to low-concentration nitrogen dioxide and ammonia diluted in air at room temperature The sensitivity is attributed to the electron transfer from the reduced GO to adsorbed NO_2 & ammonia which leads to enriched hole concentration and enhanced electrical conduction in the reduced GO sheet.

4. Summary & Concluding Remarks

This review has highlighted the chemical sensors e.g. gas sensors and electrochemical sensors using nanocrystalline materials. Especially, the nanotubes and nanowires of oxides, silicon and carbon have been focused. Various application possibilities of the nano-based chemical sensors have been discussed with the adequate citations of the literature. The nano chemical sensors can serve the need of different aspects of the human society like medical, food, environment and safety. The reliable automatic sensors based on nano materials and nano devices are possible to be fabricated with an economic viability. The different mechanisms of operations of the nanomaterial based chemical sensors have been discussed briefly. The merits and limitations of nanomaterials for the fabrications & operations of the chemical sensors have been discussed and the advantages of the nanomaterials for chemical sensing have been clarified with examples. In view of its recent importance and applications in the field of chemical sensors carbon nanotube (CNT) & its derivatives have been discussed in details in a separate section. The special activity on graphene based sensors has also been cursorily discussed. The principle of operations of each type of sensors with figures, mathematical relations and chemical equations, as applicable, has been presented in this chapter.

This review has revealed the importance of nanomaterials in enhancing the chemical sensing properties of different functional materials. The material property in nanoscale phase shows some exceptional chemical sensing behaviour and it is explained from basic concepts of chemistry & physics. It has been observed that the poor selectivity of chemical gas sensors cannot be substantially improved by using nanomaterials unless the artificial neural network (ANN) is applied. However, more intense research down to the molecular and atomic level can largely solve the selectivity problem of the chemical sensors and indeed, there is a global alertness on this issue.

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