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Survey of the Application Nanoscale Material in Chemical Sensors

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1. Introduction

Sensors and sensor arrays for the detection of chemical and biological substances have attracted much attention in recent years. The ultimate goal is to fabricate sensors that can determine the presence of a wide range of substances at relevant concentration levels with sufficient selectivity and sensitivity. Such research would ultimately produce technology that could be applicable in many segments including food processing, environment alremediation, agriculture, medical diagnostics and defense. The main requirements besides selectivity and sensitivity are fast response, low fabrication costs, robustness and portability. Hence intensive research activities around the world are focused on developing new sensing materials and technologies (Fam et al., 2011, Sinh et al., 2006). With the development of nanotechnology, there is a growing demand for advanced electronics based on functional nanomaterials. To date, various nanomaterials have been investigated from both fundamental and practical perspectives, and their unique chemical and physical characteristics have been continuously discovered. Important characteristics and the quality parameters of nanosensors can be improved over the case of classically modeled sensors merely reduced in size.

2. Nanostructure sensors

2.1 Carbon nanotube sensors

Since discovery, carbon nanotubes (CNTs) (in 1991) have been extensively explored for numerous applications. Of all the nanomaterials reported, carbon-based nanomaterials like fullerenes, graphene and carbon nanotubes (CNTs) show a huge potential in bringing sensor technology to the next level. Of these carbonaceous materials, CNT stand out as the most promising material for deployment in electronic sensing platforms due to its superior chemical and electronic properties. Furthermore, CNT possess a great potential for being employed both as a part of the transducer element as well as a functional receptor element in an electronic device. Despite the potential associated with CNT-based sensors, the efforts devoted to commercialization are still being limited by the challenges involved in CNT synthesis and device fabrication. Over the years, several attempts have been made to address these issues, for example, controlled synthesis of CNT. Although the scientific breakthroughs are numerous in this area, much of the CNT sensor research still remains at a proof-of-concept and/or prototype stage (Fam et al. 2011, Sinh et al., 2006).It could be observed from patents filed over the recent years on CNT array sensors (Kovtyukhova et al., 2003) that CNT platform has the potential to become mercialized in the near future as challenges in device fabrication and understanding of the functioning mechanisms are being overcome. This is further evidenced by a recent report on commercializing CNT based sensors introduced by Nano mix Inc., emphasizing on fabrication approaches for obtaining uniform devices for detection of biomolecules and toxic substances resulting from industrial emissions. There are generally three techniques used for producing CNTs, namely, carbon arc-discharge technique (Ebbesen et al.1992), laser-ablation technique (Thess et al.1996) and growth by either (CVD) or other methods (Jose-Yacaman et al.,1993, Li et al.,1996, Star et al., 2004).

2.1.1 Sensor fabrication

The synthesis of isolated carbon nano tubes with uniform outer diameters and ordered spacing over wafer-scale areas was investigated for fabrication of nano-electrode arrays on silicon wafers for field emission and sensor devices. Multi-walled carbon nano tubes (MWCNTs) were grown on TiN electrode layer with iron catalyst patterned by nano-imprint lithography (NIL), which allows the precise placement of individual CNTs on a substrate. The proposed techniques, including plasma-enhanced chemical vapor deposition (PECVD) and NIL, are simple, inexpensive, and reproducible methods for fabrication of nano-scale devices in large areas. CNT sensor device fabrication essentially integrates the CNT morphology obtained via the chirality, diameter and length separation using controlled synthesis techniques with a supporting substrate and electrode interconnections in a transistor (Fig. 1) or resistor configuration.

The ability to sense lies in the nature of the interaction between the sensitive material and the analyte; whether the analyte molecules bind specifically to the sensitive material and hence change its intrinsic properties, electronic or mechanical. Due to the difficulty in optimization of such a device, commercialization is still elusive one notable contribution to commercialization could be found in the works of Gruner and Star et al.

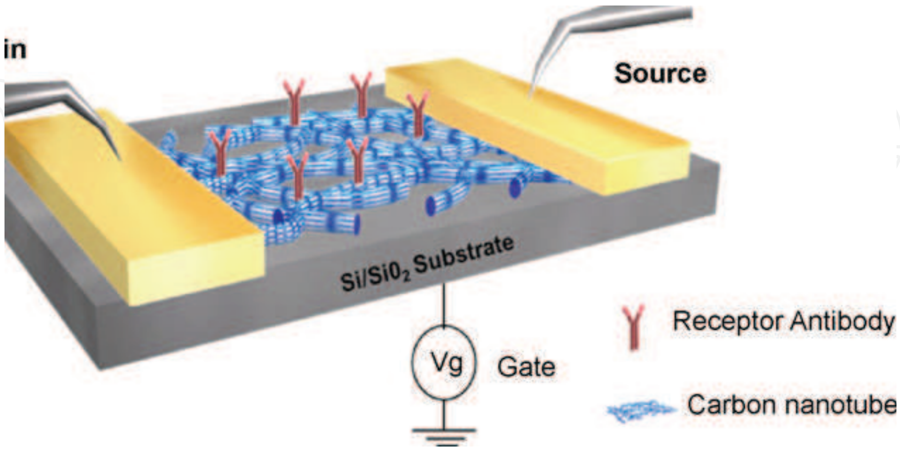

Fig. 1. Schematic of CNT transistor device (Star et al., 2004)

The catalyst patterns were defined by an array of circles with 200nm in diameter, and variable lengths of pitch. The nano-patterned master and Fe catalyst were observed with good pattern fidelity over a large area by atomic force microscope (AFM) and scanning electron microscopy (SEM) (Fig.2). Nano-electrodes of MWCNTs had diameters ranging from 50nm to 100nm and lengths of about 300 nm. Field emission tests showed the reducing ignition voltage as the geometry of nano tube arrays was controlled by catalyst patterning. These results showed a wafer-scale approach to the control of the size, pitch, and position of nano-electrodes of nanotubes for various applications including electron field-emission sources, electrochemical probes, functionalized sensor elements (Chang et al.,2011).

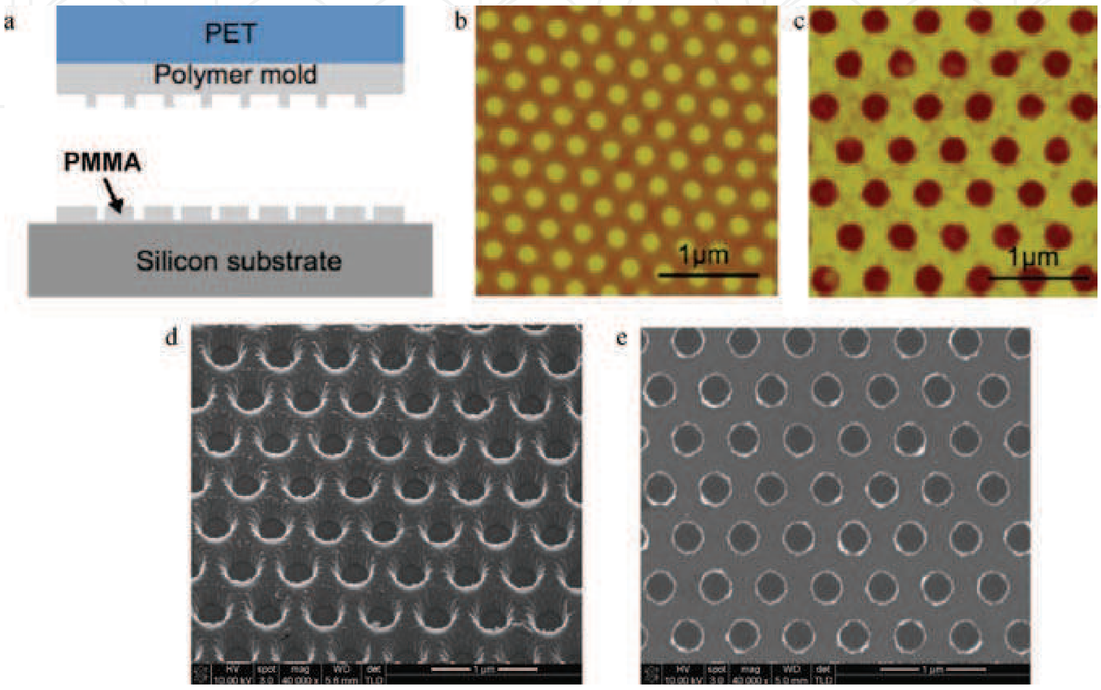

Fig. 2. (a) Schematic of UV curable resin mold. AFM images show the surface morphologies of polymer mold upper part (b) and bottom part (c). SEM images show (d) the deposition layer of Fe catalyst on a nano-patterned substrate and (e) nano-patterned Fe catalyst dots after lift-off(Chang et al., 2011).

Electrochemical (EC) sensing approaches have exploited the use of carbon nanotubes (CNTs) as electrode materials owing to their unique structures and properties to provide strong electrocatalytic activity with minimal surface fouling. Nanofabrication and device integration technologies have emerged along with significant advances in the synthesis, purification, conjugation and biofunctionalization of CNTs. Such combined efforts have contributed towards the rapid development of CNT-based sensors for a plethora of important analytes with improved detection sensitivity and selectivity. The use of CNTs opens an opportunity for the direct electron transfer between the enzyme and the active electrode area. Of particular interest are also excellent electrocatalytic activities of CNTs on the redox reaction of hydrogen peroxide and nicotinamide adenine dinucleotide, two major by-products of enzymatic reactions.

This excellent electrocatalysis holds a promising future for the simple design and implementation of on-site biosensors for oxidases and dehydrogenases with enhanced selectivity. To date, the use of an anti-interference layer or an artificial electron mediator is critically needed to circumvent unwanted endogenous electroactive species. Such interfering species are effectively suppressed by using CNT based electrodes since the oxidation of NADH, thiols, hydrogen peroxide, etc. by CNTs can be performed at low potentials (Chang et al., 2011).

2.1.2 Binding of CNTs with polymer

CNT reinforced polymeric matrix nanocomposites are prepared by polymerization of poly (methyl methacrylate) and polystyrene. This typical procedure includes the admixture of CNTs and the polymers, drying of the mixture and dissolving it with toluene. A uniform suspension of CNTs (up to 10 mg/mL) can be prepared using carboxymethylcellulose or kappa-carrageenan, which may wrap around CNTs. The strategy based on kappa-carrageenan-CNT network is used for entrapping GOx in a stable manner to form a biosensing scheme for detection of glucose (Kumar Vashist et al., 2011).

2.1.3 Polymer coated carbon nanotube-based gas sensors

For polymer coatings of nanotubes, similar to SWNT film formation, drop casting can be used. A polymer solution is placed onto a SWNT film and the solvent is allowed to evaporate. While simple, this technique also demonstrates similar reproducibility and uniformity problems to the drop casting of SWNT films.

Another method is the formation of a SWNT–polymer composite. Instead of coating the SWNTs with a polymer, the SWNTs are embedded in the polymer film, which helps with film uniformity and sensor selectivity. However, the deposition of the SWNT–polymer composite film is typically conducted with drop casting, and does not necessarily improve reproducibility. Chemical functionalization improves reproducibility of the polymer film formation, but chemically modified SWNTs can ultimately degrade sensor performance and significantly raise the recovery time of sensors. Finally, electropolymerization was selected as a simple and promising way for coating SWNT films with polymers. In this technique, the polymer film thickness can be controlled by the amount of charge applied during the process, while the uniformity and morphology of the polymer can be tuned by the monomer concentration, pH, ionic strength, and electrical parameters (Field et al., 2010).

2.1.3.1 Sensor fabrication

Following Fig. 3a, a 2.00mm diameter circle of SWNT-MCE membrane was removed from the vacuum filtered film using a hole punch (Harris, Uni-Core), as seen by the holes in Fig. 1b, and transferred to a sensor surface. The sensor substrate was made from a 100mm Silicon wafer, on which a 500nm thermal oxide layer was grown. On the wafer, 170Å chromium and 1000Å gold layers were deposited by DC magnetron sputtering (~10−2 Torr of argon background pressure) and patterned via standard lift-off photolithography. The exposed SiO2 was treated with 1% 3-aminopropyltriethoxysilane (APTES) (Gelest, Inc.) in acetone to increase the interaction between the SWNT film and sensor surface (Field et al., 2010).

Fig. 4c shows a SWNT-based sensor after nanotube transfer and deposition from the MCE membrane. In the center of the sensor, a ~2mm diameter dark circle can be seen of a 4.00 mg/L SWNT film (Field et al. 2010).

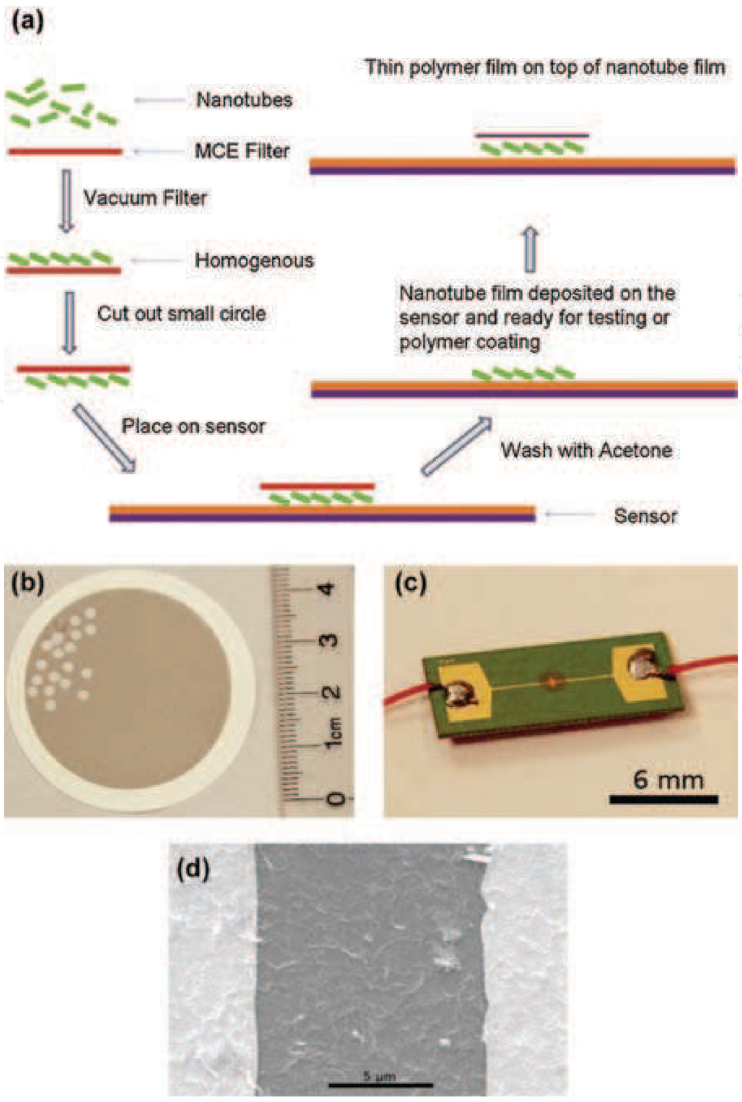

Fig. 3. (a) A flow chart of the fabrication process for the SWNT-based chemi-resistor, (b) a photograph of a vacuum-filtrated SWNT film on a 47-mm diameter MCE membrane,using 25mL of 4.00 mg/L SWNT solution (2-mm diameter circles punched out for subsequent transfer to sensors), (c) a photograph of a SWNT sensor on silicon substrate with 500nm thick thermal oxide and 100nm thick gold electrodes (a dark circle of 2-mm diameter representing a transferred SWNT film), (d) a SEM image of the SWNT film on the 10µm gap between the electrode(Field et al. ,2010).

The relatively high reproducibility of the sensor fabrication process allowed for the response testing to be conducted in a series of three batches. As an example, the response for a sensor coated with N-MP and exposed to various concentrations of DMMP can be found in Supplementary material. It is seen that different polymer coated SWNT sensors would help to produce diverse modulated sensitivity profiles against several gases. The results can be extended to establish a comprehensive histogram of modulated response to each analyte. The response from each polymer coating in an array creates a unique molecular signature that can be used to detect and identify unknown gas molecules. Efforts are underway to establish a library of responses and improve the polymer coatings to maximize the detection and identification power of an array of polymer coated SWNT sensors (Field et al., 2010).

2.1.4 Other strategies

Clay and ceramic materials are also useful for modification of CNT based electrodes. NiO/Na-montmorillonite (clay) binds to CNTs and is used to modify GCE using a Nafion solution (Zhao et al., 2011). A CNT ceramic composite is prepared by admixing CNTs and silica sol. Toluidine blue (Tb) adsorbs on CNTs to improve the dispersion of CNTs in water. The Tb-CNT suspension is then dropped on the electrode surface for subsequent modification with horseradish peroxidase. Ionic liquid (IL) modified CNTs are highly resistant towards biomolecular fouling and have high electron transfer kinetics. The IL/CNT modified electrode is prepared by adding CNTs to trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl)-imide and dispersing in DMF with ultrasonication (Hsu et al.,2009). The IL-CNT suspension is dropped on the electrode surface for subsequent electrodeposition of metallic nanoparticles.

Ferrocene and its derivatives are widely used as artificial mediators of electron transfer in CNT-EC sensors owing to their relatively low molecular mass and reversible voltammograms. $NaCNBH_3$ is added to a suspension of aminated MWCNT and ferrocene carboxaldehyde (FcCHO) with stirring for 24 h. The resulting MWCNT-FcCHO nanocomposite is used to modify GCE (Xiao et al.2009).

2.1.5 CNT sensors applicaction

Biomolecular sensing (Amino acids)

CNT-EC sensors have been extensively reported for biomolecular sensing, especially for the detection of glucose and neurotransmitters. There are also many reports where researchers have successfully demonstrated the detection of proteins, DNA, biomarkers, cells, microorganisms and other biomolecules.

A MWCNT-Cu_2O paste electrode can detect 19 amino acids. Combined capillary electrophoresis with amperometric detection is used for the detection of various amino acids such as arginine, tryptophan, histidine, threonine, serine, and tyrosine, which had high oxidation current responses. A rapid glutamate biosensor based on the oxidation of nicotinamide adenine dinucleotide (NADH) is prepared by immobilizing glutamate dehydrogenase (GLDH) on the SWCNT thionine mediator (Fam et al., 2011).

Besides sensing applications, the use of CNTs as catalyst support to construct functionalized nanocomposite interface for oxidation of NADH suggests great potential applications for the design of biofuel cells and bioelectronics.

Carbon nanotubes humidity sensor

A multiwall carbon nanotubes (MWCNTs) humidity sensor based on alternating current (AC) testing is made, and its frequency characteristic is studied. The mechanism of the sensor response to RH under alternating current testing can be interpreted by the theory of capillary condensation and dielectric physics, and the electrical model of the sensor is explored by both experimental and theoretical analysis. The stability, repeatability and response time of the sensor are investigated in details. Experiment results show that the sensor under AC testing demonstrates higher sensitivity and better reversibility (Zhao et al., 2011).

Carbon nanotubes based gas sensor

Besides liquid phase applications, the electrical resistivities of SWCNTs change sensitively on exposure to NO_2, NH_3 and O_2 with very fast response times compared to metal-oxide and polymer based sensors. This feature might offer an opportunity for the development of gas phase sensors using CNTs. On this line of argument, various configurations employing CNTs as chemo-sensitive overlay have been impressively studied to fabricate innovative gas and vapor phase chemical sensors (Someya et al.2003, Penza et al. 2004, 2005, Santhanam et al., 2005). In particular, the peculiarity of SWCNTs to change their optical properties due to the adsorption of environmental pollutant molecules was for the first time demonstrated in 2004. In that case, nano-scale thin films of SWCNT bundles were transferred on the optical fiber termination by means of the Langmuir–Blodgett (LB) technique and used as sensitive coatings for the development of volatile organic compounds (VOCs) optical chemo-sensors. The feasibility of exploiting novel chemo-sensitive coatings based on cadmium arachidate (CdA)/singlewalled carbon nanotube (SWCNT) composites for the development of high performance optical chemo-sensors has been experimentally investigated and proved(Consales et al., 2009).

Recently, several groups reported that CNT could be used as a miniature chemical sensor (Trojanowicz, 2006). Kong et al. demonstrated that the conductance of semiconducting SWNT (S-SWNT) could be substantially increased or decreased upon exposure to gaseous molecules, such as NO_2 or NH_3 (Kong et al. 2000). The presence of gas molecules could be determined by monitoring the electrical resistivities of nanotubes. The individual S-SWNT sensors were very small and had good sensitivity as high as 103 at room temperature. The nanotube sensors have shown to several have advantages over presently available metal oxide and polymer sensors. The reversibility of the nanotube sensor could be achieved by slow recovery under ambient conditions or by heating at a high temperature. Collins's group reported that the isolated semiconducting SWNT could be converted into apparent metals through exposure to oxygen at the room temperature (Collins et al.,2000). It was demonstrated recently that a thermoelectric “nano-nose” could be built from tangled bundles of SWNTs (Adu et al., 2001). The response was specific and gases such as He, N_2, H_2 could be easily detected. Experiments showed the thermoelectric power and resistivity of a bundle of SWNTs varied with different gases, such as He, N_2, H_2, O_2 or NH_3. In the design of gas sensors, some unusual electronic, mechanical and thermal properties of CNTs are utilized and the unique feature characteristics of most reported sensing transduction modes related to conjugated polymers and carbon nanotubes have previously discussed (Dai et al., 2002). The sensors developed so far have used different mechanisms of interacting analytes with CNTs, as well as different modes of preparing CNTs in sensors. For constructing gas sensors, most often, changes in the electrical properties of CNTs as result of their interaction with analytes are used.

2.1.6 Technical challenges and future directions of CNT

Numerous reports on evaluation of toxicity of CNT and its biocompatibility are indicative of the potential of CNT for commercial device fabrication. Recent years have witnessed a growing number of CNT related patents emphasizing commercialization possibilities. A large number of research groups are actively pursuing CNT related research to study their interaction capabilities with potential analytes. The relatively less expensive CNT related devices and fabrication processes also have attracted interest from other field of science and technology. In summary, there is a huge potential for CNT in the field of bio and chemical sensors. Numerous reports on remarkable sensing properties of nanotubes would envisage feasible commercialization strategies. Although ultra-sensitive detection methodologies and detection capabilities at fM concentration levels have been reported, substantial research efforts are still needed to eliminate high matrix interference from real samples.

2.2 Other nanostructure sensors

As far as chemical sensing is concerned, it has been known, from more than five decades, that the electrical conductivity of metal oxides semiconductors varies with the composition of the surrounding gas atmosphere. The sensing properties of semiconductor metal oxides in form of thin or thick films other than SnO_2, like TiO_2, WO_3, ZnO, Fe_2O_3 and In_2O_3, have been studied as well as the benefits from the addition of noble metals – Pd, Pt, Au, Ag – in improving selectivity and stability.

2.2.1 ID ZnO nano-assemblies as chemical sensors

ID ZnO nano-assemblies were prepared on Al_2O_3 substrates by plasma enhanced-chemical vapor deposition (PE-CVD), and characterized in their morphology and chemical composition by field emission-scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDXS) and X-ray photoelectron spectroscopy (XPS). For the first time, the sensing performances of PE-CVD ZnO nanosystems were tested in the detection of toxic/combustible gases (CO, H_2 and CH_4), revealing very good responses already at moderate working temperatures. In particular, carbon monoxide and hydrogen detection was possible already at 100 °C, whereas methane sensing required a minimum temperature of 200 °C. The performances of the present ZnO nanosystems, that make them attractive candidates for technological applications, are presented and discussed in terms of their unique and controllable morphological organization (Barreca et al., 2010).

Various ZnO nanostructures, such as nanobelts, nanorods, and nanowires, have been grown on presynthesized SnO_2 nanobelts via a simple thermal evaporation of Zn powders, without using any catalysts, producing various heterostructures (Liangyuan et al., 2010). The evaporation temperature is the critical experimental parameter for the formation of different morphologies of these nanostructures. Room temperature photoluminescence spectra of the heterostructures show that the relative intensity of ultraviolet emission to the green band can be tuned by controlling the morphologies and sizes of the secondary-grown 1D ZnO nanostructures, suggesting that the nano-heterostructures of these nanostructures grown on SnO_2 nanobelts may have potential applications in nano-optoelectronic devices (Krishnakumar et al., 2009).

High degree of crystallinity and atomic sharp terminations make nanowires very promising for the development of a new generation of gas sensors reducing instabilities, typical in polycrystalline systems, associated with grain coalescence and drift in electrical properties. These sensitive nanocrystals may be used as resistors, and in FET(field-effect transistors) based or optical based gas sensors.

2.2.2 Applications of metal oxide nanostructures

Metal oxide gas sensors Metal oxides semiconductors are normally high gap metal oxides in which the semiconducting behavior arises from deviation of stoichiometry. They should always be regarded as compensated semiconductor: cation vacancies are acceptors, yielding holes and negative charged vacancies, shallow states made up of oxygen vacancies acts as n-type donors, since the bonding electrons on the adjacent cation are easily removed and donated to the conduction band.

The termination of the periodic structure of a semiconductor at its free surface may form surface localized electronic states within the semiconductor band gap and/or a double layer of charge, known as a surface dipole. As for conduction, metal oxide gas sensors are generally operated in air in the temperature range between 500 and 800 K where conduction is electronic and oxygen vacancies are doubly ionized and fixed. In quasi 1D gas sensors the current flows parallel to the surface. When the nanowire is fully depleted, carriers thermally activated from surface states are responsible for conduction. Indeed when considering nanowires bundles, the conduction mechanism is dominated by the inherent intercrystalline boundaries at nanowires connections – like in polycrystalline samples – rather than by the intracrystalline characteristics; the intergranular contact provides most of the sample resistance (Lupan et al., 2009).

The metal semiconductor junction that forms at the interface between the layer and the contacts can play a role in gas detection, enhanced by the fact that the metal used for the contact acts also as a catalyst. The contact resistance is more important for single nanowires since it is in series to the semiconductor resistance that for bundles where it is connected to a large number of resistances.

The development of sensitive and reliable gas sensing devices for the detection of flammable/toxic chemical agents, such as CO, H_2 and CH_4, has gained an increasing attention for safety, energy and environmental applications. In particular, in spite of various works, continuous efforts are devoted to the development of low-cost, lightweight sensors for H_2 detection wherever hydrogen is produced, stored or used, including industrial plants, spacecrafts and fuel cells vehicles. Furthermore, the detection of leakages of flammable/explosive fuels, like methane, and toxic combustion products, such as CO, is of great importance to control domestic gas boilers, mining environments and combustion processes in automotive engines and industrial plants (Mukherjee et al. 2009, Bhattacharyya et al., 2008).

Hydrogen, when absorbed by a metal, occupies interstitial sites in the metal lattice causing this lattice to expand and thereby changing the physical properties of the metal. Micro-fabricated palladium coated cantilevers utilize the expansion of palladium following hydrogen absorption as the detection principle. These sensors consist of a palladium film coated on one side of a cantilever. However volume expansion on absorption of hydrogen is prohibited by the substrate on which the film is coated and the induced stresses are transduced into the mechanical bending or curvature of the cantilever. There is a limited amount of research published on cantilever hydrogen sensors and one problem associated with this type of sensor arises from interfacial sliding, delamination and even detachment of the palladium film as a result of expansion/contraction induced weakening of the palladium/ substrate adhesion. The initial adhesion strength between the palladium film and the underlying substrate depends on the method used to deposit the palladium film. It has been shown that palladium films fabricated by sputtering bombardment have superior adhesion characteristics and ultimately exhibit superior hydrogen detection characteristics as a result of efficient mechanical transduction (Chou et al. 2008). Further enhancement of the Pd adhesion by the fabrication of trenches in the surface of the cantilever beams led to improve hydrogen sensing down to 50 ppm and faster response.

Another novel mechanical hydrogen sensor is described and comprises a micromachined cantilever fabricated out of the cleaved edge of an optical fiber (Iannuzzi et al.,2007).

The sensing tungsten nanowire is synthesized by focused ion beam-chemical vapor deposition (FIB-CVD) using $W(CO)_6$ precursor gas on batch-fabricated microelectrodes. The nanowire measures 10μm in length and 150 nm in diameter, and is suspended 50μm above the wafer substrate connecting two microelectrodes to enhance the exposure of nanowire surface to target gas molecules for improved chemisorptions. The nanowire is then functionalized by palladium–platinum (Pd–Pt) sputtering process to be sensitive to the hydrogen molecules. The significant increase of nanowire resistance is observed whenever it is exposed to hydrogen molecules, and the resistance is recovered to the original value after hydrogen molecules are purged out. The experimentally characterized hydrogen sensor shows 11.52% increase of resistance to the exposure to 1% (10,000 ppm) hydrogen and 99% nitrogen gas mixture at room temperature and atmospheric pressure. The lowest hydrogen concentration measured is 0.001% (10 ppm) with 0.58% corresponding resistance increase. The schematic view and electric circuit configuration of the hydrogen sensor based on a suspended tungsten nanowire bridge on microelectrodes is shown in Fig. 4(a). The tungsten nanowire is synthesized 50μm above the substrate on top of batch-processed microelectrodes. The microelectrodes are fabricated on a heavily doped silicon-on-insulator (SOI) wafer with 50μm device layer and 1μm buried oxide using single photolithography step, deep reactive ion etching (DRIE) and the following wet etching in hydrofluoric acid. Scanning ion microscope (SIM) image in Fig4 (b) shows the nanowire bridge connecting two microelectrodes with bonded aluminum wire for signal measurement (Choi et al., 2009).

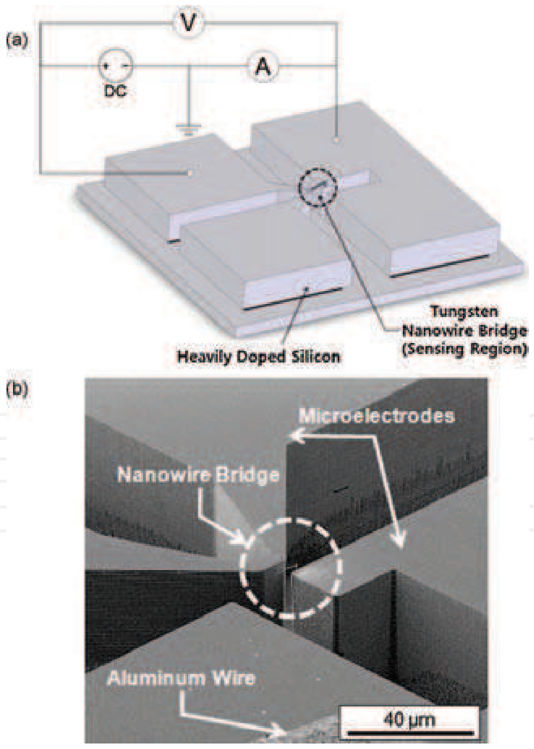

Fig. 4. (a) Schematic view of suspended single tungsten nanowire bridge hydrogen sensor. The nanowire is synthesized by FIB-CVD on microelectrodes and constant current is applied between the microelectrodes and through the nanowire to monitor the voltage drop when it is exposed to hydrogen gas. (b) SIM image of microelectrodes and suspended single tungsten nanowire bridge with bonded aluminum wire (Choi et al., 2009).

Focused ion beam-chemical vapor deposition (FIB-CVD) is an alternative to fabricate nanostructures on desired position with controllable dimensions. The most common application of FIB has been repairing and wiring the defected semiconducting circuits. Recently, efforts were undertaken to fabricate three-dimensional nanostructures using FIB.

2.3 Nano-grass polyimide-based humidity sensors

This section deals with a micro-capacitive-type relative humidity sensor with nano-grass polyimide as a dielectric sensing material. Humidity sensor achieves key performance indices such as quick response, high sensitivity, and stability enabled by the modification of polyimide into nano-grass morphology where the dimension of a typical individual pillar is 387nm×40 nm. A low hysteresis operation is also achieved by integrating a micro-heater in the sensing area. The nano-grass morphology is created with an oxygen plasma treatment on polyimide surface which increases surface to volume ratio by more than 280 times larger than that of a simple flat-film. This amplification of the surface to volume ratio leads to the rapid adsorption and desorption of water into the sensing material. Furthermore the oxygen plasma treatment introduces a carbonyl group that facilitates an enhanced affinity of the polyimide surface to water molecules. XPS analysis is used to confirm the emergence of carbonyl groups as a result of the treatment. The total response time of a nano-grass sensor is 11 s which is improved by about 2.5 times than a normal flat-film sensor. The sensitivity of the nano-grass sensor is 0.08 pF/%RH (relative humidity) which is improved by 8 times compared with the flat-film one. In stability test for 200 h, the signal of the nano-grass sensor is fluctuated ±1.0%RH (Lee et al., 2011).

2.3.1 Sensor structure

Humidity sensor consists of interdigitated gold electrodes and a polyimide layer coated on top as a moisture sensing material. Since a pure capacitive detection was used in our configuration, a leakage current path between the electrodes was prevented by a SiO_2 passivation layer between the electrode (Au) and the sensing material (polyimide). The size of the whole device was 6mm×3mm, and the typical dimension of sensing polyimide area was 2.3mm×1.0mm×2μm. The interdigitated electrodes consist of nine parallel fingers, 1.9mm long, 0.2μm thick, 20μm in width, and 50μm apart from each other (Fig.5,6). A heater pattern was also included which was 20μm in width, 0.2μm thick, and 12.8mm in length, running along the centre of the gap. The total resistance of the heater line was 78Ω (Lee et al. ,2011).

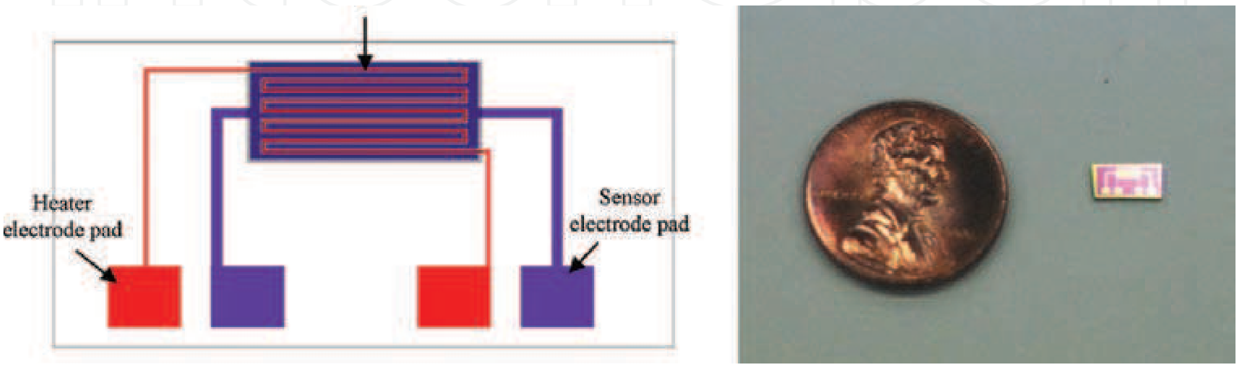

Fig. 5. Mask pattern and photograph of device(Lee et al. ,2011).

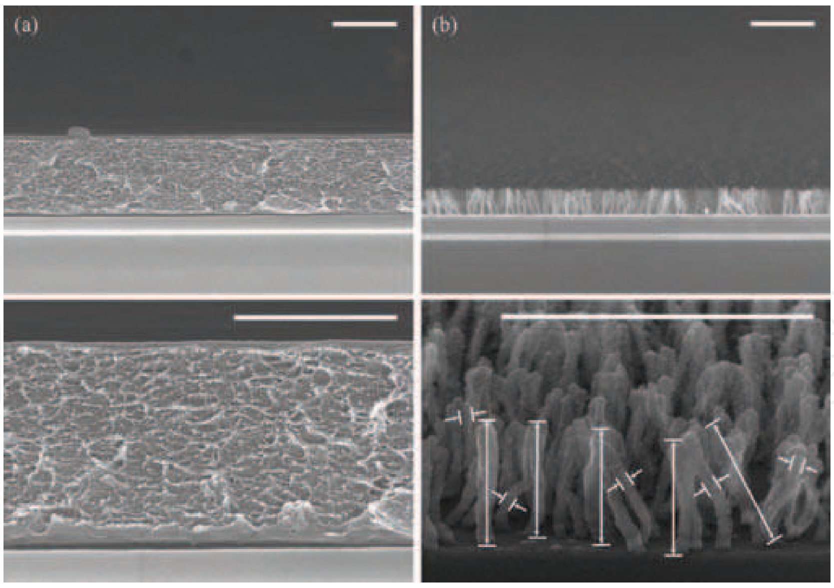

Fig. 6. Polyimide nano-grass produced by an oxygen plasma (scale bar; 1μm): (a) flat-film polyimide, (b) nano-grass polyimide (Lee et al. ,2011). .

2.3.2 Device fabrication

Fig. 7 shows the fabrication process of polyimide-based humidity sensor. The process began with the wet oxidation of 2000Å silicon oxide on a silicon wafer as an insulating layer (Fig.7a). Cr/Au (100/1000 Å) layers were e-gun deposited on the substrate, followed by a wet etching to pattern the sensing electrodes and the heater configuration (Fig. 6b). TEOS (Tetra-ethyl-orthosilicate) was deposited on top of the electrodes as a passivation layer with PECVD. Polyimide was spin-coated at 5000 rpm, for 60 s on the substrate as a sensing layer. The polyimide layer was patterned by using a wet etching with a photoresist as an etching mask. Since the polyimide could be directly etched with the diluted developing solution, the developing and etching was carried out simultaneously. After removing the photoresist, the polyimide layer originally shows flat-film morphology (Fig. 7e). A reactive ion etching was further used to modify the flat polyimide into the nano-grass (Fig. 7f). Fig.7 shows the fabrication process of polyimide-based humidity sensor. The process began with the wet oxidation of 2000Å silicon oxide on a silicon wafer as an insulating layer (Fig. 7a).

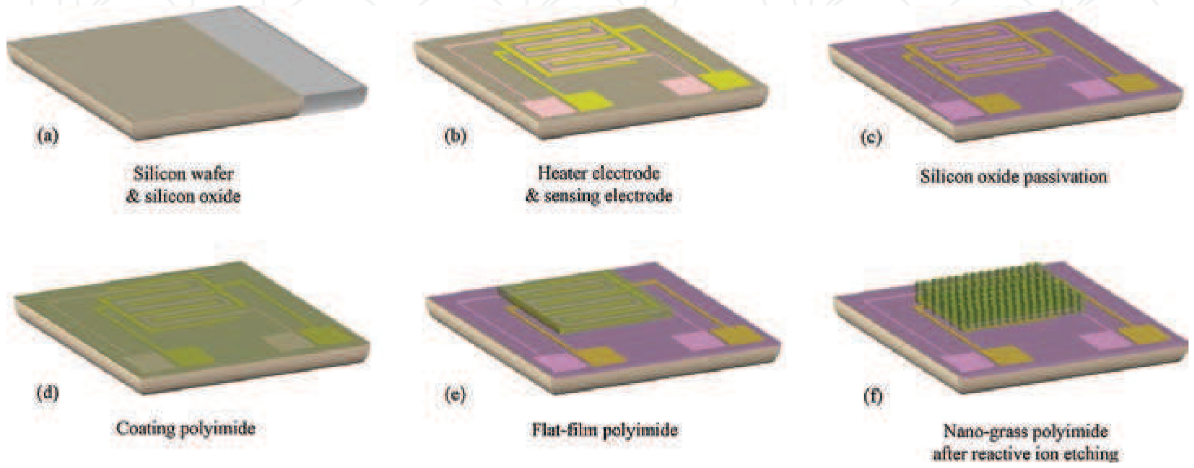

Fig. 7. Fabrication process of device (Lee et al., 2011).

A humidity sensor with high performance compared to a normal flat film type humidity sensor was developed with an increased surface area and water affinity on a nano-grass polyimide morphology enabled by a plasma etching. The nano-grass morphology has the estimated surface to volume ratio 280 times larger than that of the flat-film surface, resulting in the high sensitivity and efficient adsorption of moisture. XPS spectra indicated the increase of carbonyl groups on the plasma treated polyimide surface. The increase of carbonyl groups is responsible for further increasing the sensitivity to moisture. A heater was used to reduce the hysteresis of our nano-grass sensor. The nano-grass sensor demonstrated a clear improvement over the normal flat-film sensor in key specifications such as quick response and sensitivity, low hysteresis, and longterm stability. According to our analysis with the model equation which combined the Looyenga and the Dubinin's equations, the nano-grass sensor appears to have larger free energy of adsorption and maximum volume fraction of water than those of the flat-film sensor. This enhanced performance together with a possibility for an array fabrication may enable many new applications, e.g., a fine real-time tracking of the relative humidity distribution in a fuel cell stack (Lee et al., 2011).

2.4 Gas sensor device fabrication and testing

The schematic view of a hydrogen sensor based on Pd modified graphene is shown in Fig. 8a. CVD grown graphene with a typical size of 3mm×4mm was transferred onto a highly doped Si wafer covered by a 300 nm-thick SiO_2 film. The graphene sample on SiO_2/Si was then decorated with a thin Pd film (1nm thickness) using electron beam evaporation. To define the contacts, Ti/Au (5 nm/100 nm) films were also deposited by electron beam evaporation through a shadow mask. Subsequently, the sensor sample was assembled into a chip carrier by wire bonding, as shown in Fig. 8b were demonstrated on Pd-decorated CVD graphene films. The hydrogen sensors show high sensitivity, fast response and recovery, and are usable for multiple cycles. The mechanism of hydrogen detection can be attributed to carrier density in graphene induced by PdHx (Wu et al. ,2010).

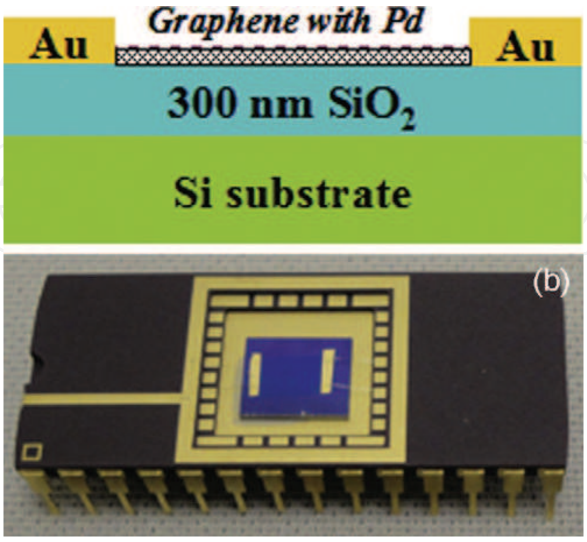

Fig. 8. (a) Schematic cross-sectional view of graphene deposited with Pd nanoparticles on SiO_2/Si substrate for H_2 sensor. (b) Photograph of a typical H_2 sensor device. The size of SiO_2/Si substrate is about 1 cm (Wu et al., 2010).

2.5 Diamond nano particles

Modified diamond nano particles (DNP) are investigated as sensitive coatings for use with Surface Acoustic Wave (SAW) transducers. DNP were surface treated (e.g. hydroxylation, hydrogenation) to enhance their affinity to specific compounds such as nitro-aromatic compounds, nerve-agent stimulant, or toxic gases. They were deposited onto SAW transducers by a layer-by layer deposition method to assess their performances for chemical vapor sensing. The DNP coated sensors were tested towards dinitrotoluene (DNT), dimethyl methyl phosphonate (DMMP), ammonia (NH_3) and relative humidity (RH). The sensors showed high sensitivity to the target compounds, good repeatability and low detection limit at sub-ppm levels, at room temperature. SAW sensors are promising for the detection of toxic chemicals due to their extremely high sensitivity. Nevertheless the sensitive coating deposited on such transducers is a limiting element. Indeed in most cases the sensitive coatings are based on polymers that are generally difficult to deposit homogeneously onto the transducer's surface .The use of these transducers requires a strict control of the coatings' properties in terms of thickness, uniformity, viscosity and film adherence in order to obtain reliable performances. However, the deposition methods that may potentially satisfy these conditions are limited to some polymer/surface systems with specific properties (Chevallier et al., 2011).

The DNP coated sensors were tested towards dinitrotoluene (DNT), dimethylmethylphosphonate (DMMP), ammonia (NH_3) and relative humidity (RH). The sensors showed high sensitivity to the target compounds, good repeatability and low detection limit at sub-ppm levels, at room temperature.

The diamond coatings' surface was either oxidised or reduced to see the effect on the response to ammonia gas, ethanol, DNT or DMMP vapours exposures. The sensors were generally very sensitive to the target chemicals and the response fully reversible. Oxidation of the surface promoted hydrogen-bond formation and therefore enhanced the response to most vapours under test. Even though the sensors were not very selective, demonstrated the suitability of DNP coatings as stable and reliable sensing interface. This opens up wide opportunities for immobilizing more selective and highly sensitive chemical/biochemical receptors onto SAW transducer surfaces via strong covalent binding of those receptors on diamond nanoparticles deposited homogeneously on the SAW sensors surfaces. Modified diamond nanoparticles (DNPs) as an alternative sensitive coating that could solve some of the issues encountered with other known sensitive coatings.

Indeed, DNPs may be found in nanometer sizes and can be deposited as single or multiple layers on a variety of sensor surfaces with uniform thicknesses and high surface area, which is in favour of high sensitivity. DNPs feature also other attractive properties for chemical detection: on the one hand they are mostly made of sp^3 carbon which is very stable in time; it is intrinsically inert hence it can be considered as a stable sensor platform onto which specific receptors are immobilized. On the other hand the carbon terminated surface of diamond offers wide perspectives from organic chemistry and biochemistry for strong attachment of specific receptors on the diamond surface via covalent bonding (Krueger, 2008). Those receptors will be chosen for their high affinity with the target species that need to be detected. The sensor response will then be either reversible or non-reversible depending on the type of interactions between the receptor molecule and the target analyte.

The DNP coatings exposed shortly to CH_4/H_2 plasma were observed using an optical microscope in order to verify the homogeneity of the layer across the entire surface of the transducer.

2.6 Nano-structured conducting polymers

Conducting polymer (CP) nano tubes and nano wires can be prepared by physical approaches like electro spinning, chemical routes like hard physical template-guided synthesis and soft chemical template synthesis (e.g., interfacial polymerization, template-free method, dilute polymerization, reverse emulsion polymerization, etc.), and a variety of lithography techniques(Skotheim et al. ,2007).

In order to fulfill the potential applications of CP nanostructures, it is necessary to precisely address their physical properties. Electrical and optical proper ties of non-individual 1D-CP nano structures, have been extensively studied, showing unusual physical and chemical behavior due to the nano size effects. There are some key questions to be clarified, for example, the effects of the nano contacts on the electrical measurements, the tuning and the control of the electrical properties of individual nano fibers and nano tubes, etc. These questions are particularly important to develop nano devices based on individual nano wires and nano tubes (Rong et al., 2009).

Since the electrical and optical properties of CP can be reversible changed by a doping/dedoping process, CP nano structures have been widely explored as chemical sensors, optical sensors and biosensors due to greater exposure area than the conventional bulk polymers. some studies demonstrate that the gas(HCl,NH_3, NO,H_2S, ethanol, liquefied petroleum gas (Jang et al., 2005), etc.) sensors based on poly aniline or PEDOT nano fibers usually how a higher sensitivity and shorter response time because of higher surface areas (Lu et al., 2009). For example, it was found that the response times of the polyaniline nano fiber sensors exposed to chloroform, toluene and tri ethylamine were about a factor of 2 faster ,with the current variations up to 4 times larger than those of the bulk poly aniline sensors.

Drug delivery devices have flourished during the last few decades and are extensively used in various kinds of treatments. Conducting polymer-based devices have been investigated to examine how they can serve as electrically controlled drug delivery devices inside the body. One major challenge is to develop a drug delivery system that allows strict control of the ON/OFF state. In addition, such a device must be able to deliver the drug of interest at doses that are required to obtain the therapeutic effect.

Nanomaterials of conjugated polymers are found to have superior performance relative to conventional materials due to their much larger exposed surface area (Rajesha et al., 2009).

The developments in nano-structured conducting polymers and polymer nanocomposites have large impact on biomedical research. Significant advances in the fabrications of nanobiosensors/sensors using nano-structured conducting polymers are being persistently made (Maity et al., 2006, Price et al. ,2008).

The study also demonstrates the role of nano-structured conducting polymers in the emerging field of nanosensors/biosensors. A detail analysis has been carried out on the latest research advancement made in the development of nano-structured conducting polymers and polymer nanocomposites based sensors/biosensors. As the surface nano-structure becomes more demanding and complex, more synthetic methods for the construction of nano-structured materials will be required. These methods will use new nano technological approaches to conducting polymers and their applications in biomedical research. Increasing interest in and practical use of nanotechnology, especially, in conducting polymers and polymer composites have lead the researchers to the rapid development of nano sensors/biosensors with improved process ability and functionality over previously developed sensors(Maity et al. 2006, Price et al. 2008, Ma et al. 2006).

2.7 Organic thin film transistor chemical sensors

Organic thin film transistor (OTFT) chemical sensors rely on the specific electronic structure of the organic semiconductor (OSC) film for determining sensor stability and response to analytes. The delocalized electronic structure is influenced not only by the OSC molecular structure, but also the solid state packing and film morphology. Phthalocyanine (H_2Pc) and tetrabenzoporphyrin (H_2TBP) have similar molecular structures but different film microstructures when H_2Pc is vacuum deposited and H_2TBP is solution deposited. The difference in electronic structures is evidenced by the different mobilities of H_2TBP and H_2Pc OTFTs. H_2Pc has a maximum mobility of 8.6×10^{-4} cm^2 V^{-1} s^{-1} when the substrate is held at 250 °C during deposition and a mobility of 4.8×10^{-5} cm^2 V^{-1} s^{-1} when the substrate is held at 25 °C during deposition. Solution deposited H_2TBP films have a mobility of 5.3×10^{-3} cm^2 V^{-1} s^{-1}, which is consistent with better long-range order and intermolecular coupling within the H_2TBP films compared to the H_2Pc films. Solution deposited H_2TBP also exhibits a textured film morphology with large grains and an RMS roughness 3–5 times larger than H_2Pc films with similar thicknesses. Despite these differences, OTFT sensors fabricated from H_2TBP and H_2Pc exhibit nearly identical analyte sensitivity and analyte response kinetics. The results suggest that while the interactions between molecules in the solid state determine conductivity, localized interactions between the analyte and the molecular binding site dominate analyte binding and determine sensor response (Royer et al., 2011).

Group of sensor materials were characterized by their good thermal stability, high optical absorbance and functionality. Porphyrins are structurally related to phthalocyanines, with the four –CH groups in the inner porphyrin ring replacing the four meso nitrogens of phthalocyanine. Several studies have investigated differential chemical sensing by changing the central metal atom in the Por/Pc core or by changing the peripheral substituents (Wang et al. 2011, Bohrer et al. 2009, 2007) Sensing.

By analyzing the transient recovery in OTFT chemical sensors, the analyte binding kinetics can be elucidated. The t_{60} values are normalized with respect to MeOH to illustrate the consistent relative recovery times for each sensor. The relative recovery time normalizes the t_{60} for each recovery with respect to the t_{60} for MeOH. This eliminates run-to-run variations in flow rate or temperature which could influence recovery rates. Both H_2Pc and H_2TBP sensors exhibit rapid recovery following doses of weak binding analytes such as MeOH and ACN, whereas for strong binding analytes such as TMP and DMMP there is a slower recovery. The H_2TBP sensor recovery immediately following a 15.8 ppm DMMP

H_2Pc sensors show significantly shorter t_{60} for isophorone than DMMP and TMP despite having a high sensitivity to isophorone; however, anomalous recovery characteristics for isophorone in H_2Pc chemiresistors have been reported previously. It has been suggested that physisorbing analytes can interact with MPc films by preferential binding or by weak van der Waals interactions with the conjugated π system of H_2TBP and H_2Pc(Gundlach et al. 2008,). Therefore, it is possible that the meso nitrogens present in H_2Pc, and absent in

H_2TBP, contribute to sensor response and recovery. However, the fast recovery and low sensitivity for each sensor to doses of MeOH and ACN suggest that the molecular structure of the extended π system does not significantly alter sensor response (Royer et al., 2009).

OTFT device properties are highly dependent on fabrication methods which influence film electronic structure by affecting grain size and intermolecular coupling (Bohrer et al., 2009). The different surface morphologies of 100 nm H_2Pc films with T_{sub} = 25–250 °C and a solution processed H_2TBP film are shown in atomic force microscopy (AFM) images presented in Fig. 9a–e. Line profiles of a 500 nm segment are shown as insets for each image. The height scale on the line profiles is held constant to demonstrate the larger surface roughness for H_2TBP films. OTFT sensors based on solution processed H_2TBP were found to have enhanced mobilities while yielding chemical sensing properties nearly identical to OTFT sensors based on vapor deposited H_2Pc. The mobilities of the films were strongly affected by differences in film microstructure, but this had little influence on chemical sensor behavior. This is consistent with analyte binding being chiefly a function of interactions with individual molecules of the sensor film. This study suggests the feasibility of preparing nonvolatile metal coordination complex sensor arrays with solution processed films. Consistent chemical sensor response can be obtained despite dramatic changes in field-effect mobility, which implies that relative chemical sensor response is a more robust property than field-effect mobility in OTFT sensors (Royer et al., 2011).

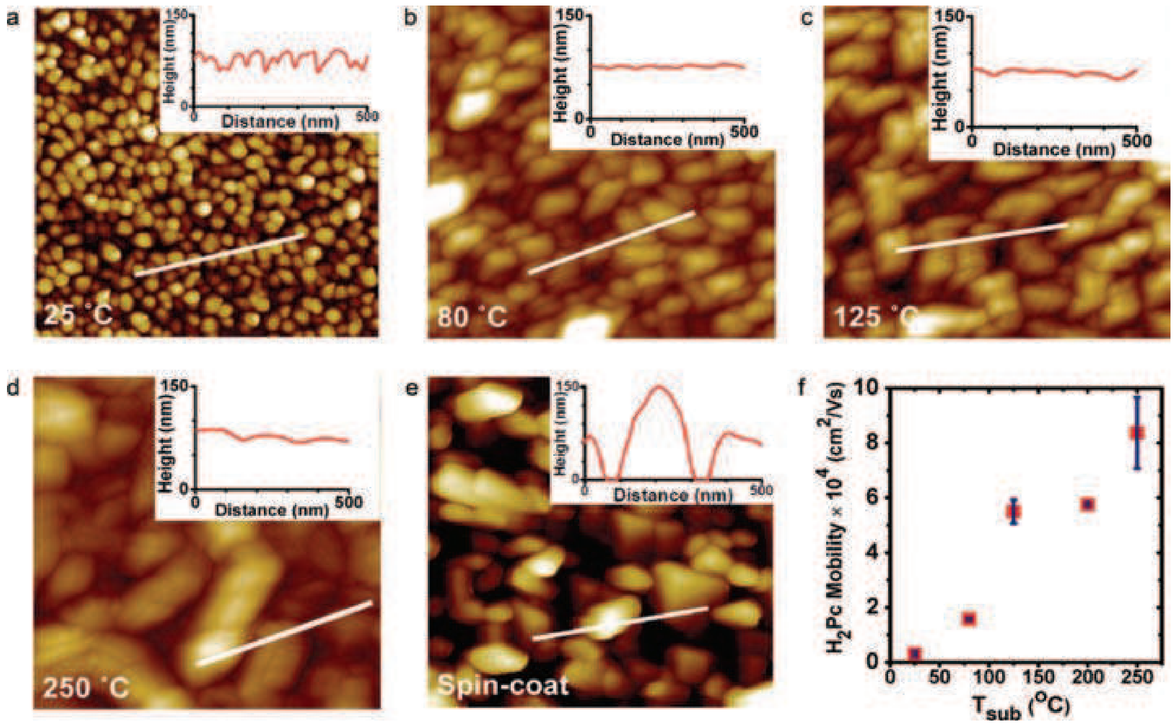

Fig. 9. H_2TBP and H_2Pc film microstructure characterization. Atomic force microscopy (AFM) images of a 1 µm × 1 µm region of 100 nm H_2Pc deposited on SiO_2 substrates held at (a) 25 °C, (b) 80 °C, (c) 125 °C, (d) 250 °C. (e) AFM image of 1 µm × 1 µm region of solution processed H_2TBP. The insets show line profiles of a 500 nm segment indicated by a white line in the image. The height scale on the line profiles is held constant to demonstrate the larger surface roughness for H_2TBP films. (f) Mobility of H_2Pc OTFTs with different substrate temperatures (T_{sub}). Some error bars are smaller than the markers (Royer et al., 2011).

2.8 Flexible chemical sensors

Flexible chemical sensors are not a new concept. Traditional chemical sensors based on conductive polymers over polymer substrates are generally flexible. However, with the advent of high-quality nanowires and nanotubes and the rapid development of flexible electronics which involves many breakthroughs in the synthesis and manipulation of these nanoscale materials, significant progress has been made in modern flexible chemical sensors.

In traditional conductive polymer chemical sensors, self-organization in many solution-processed, semiconducting conjugated polymers results in complex microstructures, in which ordered microcrystalline domains are embedded in an amorphous matrix. This has important consequences for the electrical properties of these materials, i.e. charge transport is usually limited by the most difficult hopping processes and is therefore dominated by the disordered matrix, resulting in low charge carrier mobilities ($<10^{-5}$ cm^2/V.s).

Mobility as high as 104 cm^2/V.s in SWNT has been reported (Zhou et al. 2005). Owing to the superior quality of SWNTs, high sensitivity, low detection limit and fast response time have been observed in these nanowire- and nanotube-based chemical sensors. For highly crystalline metal oxide nanowires, a few sensing reactions occurred at room temperature instead of at high temperature. Ingenious nanowire and nanotube assembly and alignment open up many possibilities for high-performance multifunctional flexible chemical sensor development. Large integrated sensors with built-in intelligence are also on the horizon. The future of flexible chemical sensors is indeed very promising.

There are a few common features in these successful results with the use of ZnO, SnO_2 and In_2O_3 metal oxide nanowires. The use of nearly single-crystalline (high-quality) nanowires appears to be essential. A small diameter (~10 nm), with a high surface-to-volume ratio, is also important for reaching high sensitivity at room temperature. The use of metal oxides for gas sensing has been extensively reviewed (Shen et al., 2009, Huang et al., 2007, Graf et al., 2006). Although the majority of the work uses polycrystalline metal oxides and requires temperature higher than 300°C, promising results based on high-quality single-crystalline metal oxides have been achieved at ambient temperature (see above). It is foreseeable that high quality metal oxide nanowires, nanotubes and possibly nanoparticles may be attached to flexible substrates and developed into flexible chemical sensors.

A Si nanowire array, prepared separately, has been transferred onto a polyethylene terephthalate (PET) substrate with use of a poly(dimethylsiloxane) (PDMS) contact printing technique. The flexible Si nanowire FETsensor can detect NO_2 down to 20 ppb. Both Si and Ge nanowires have been transferred onto hard (Si/SiO_2) and soft (Kapton, polyimide) substrates on a wafer scale through contact printing with sliding and lubrication. The process prepares nanowire arrays with high density (~8 nanowires/μm) and 95% directional alignment. Therefore, it is likely that flexible chemical sensors based on crystalline metal oxide nanowires will be developed in the future.

A new class of nanostructured plasmonic chemical sensors has been developed in recent years (Tong et al., 2005, Jiang et al., 2008). Gold and silver nanoparticles are frequently studied because they exhibit a strong surface plasmon resonance (SPR) in visible wavelength. The aggregation of these nanoparticles will result in a significant color change that serves as the basis of sensitive chemical detection. For example, the surfaces of Au nanoparticles may be derivatized with oligonucleotide and in the presence of complementary target DNA, Au nanoparticles will aggregate and change their color from red to blue. A similar approach was applied to trinitrotoluene (TNT) detection where Au nanoparticles prepared from trisodium citrate were first treated with cysteamine ($SHCH_2CH_2NH_2$). Upon addition of TNT solution, the Au nanoparticles solution turned from red to violet blue owing to TNT-induced Au nanoparticle aggregation (Fig. 10). Although these chemical sensing techniques were demonstrated in solution, it is likely that solid-state thin-film methods will be developed in the future (Tong et al., 2005).

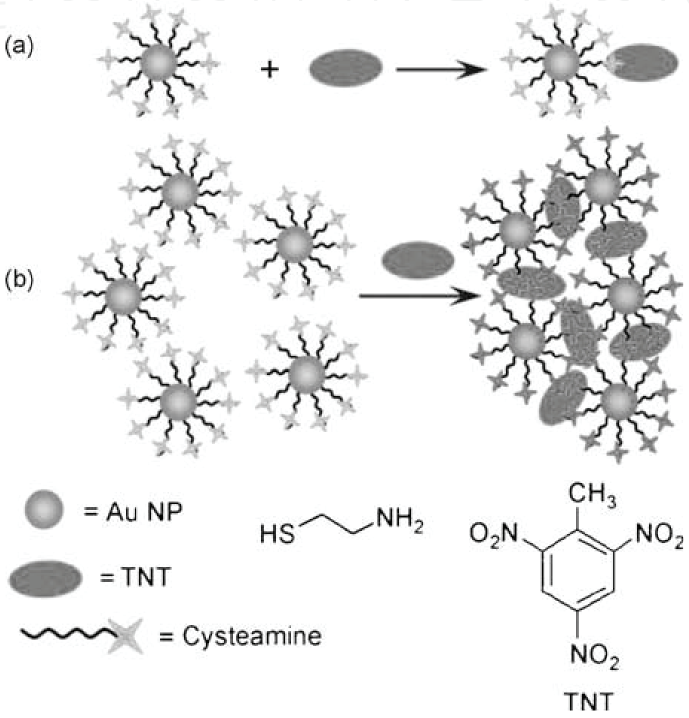

Fig. 10. Schematic drawing showing the working principle of nanoparticle-based chemical sensors. (Tong et al., 2005).

3. Conclusion

CNT have become one of the most extensively studied nanostructures because of their unique properties. CNT can enhance the electrochemical reactivity of important biomolecules and can promote the electron-transfer reactions of proteins. The remarkable sensitivity of CNT conductivity with the surface adsorbates permits the use of CNT as highly sensitive nanoscale sensors. These properties make CNT extremely attractive for a wide range of electrochemical sensors ranging from amperometric enzyme electrodes to DNA hybridization biosensors. Nevertheless, the major future challenges for the development of CNT-EC sensors include miniaturization, optimization and simplification of the procedure for fabricating CNT based electrodes with minimal non-specific binding, high sensitivity and rapid response followed by their extensive validation using “real world” samples. A high resistance to electrode fouling and selectivity are the two key pending issues for the application of CNT-based biosensors in clinical chemistry, food quality and control, waste water treatment and bioprocessing.

Diamond nano-wires can be a new approach towards next generation electrochemical gene sensor platforms. DLCs have also been applied to electrochemical measurements as electrode materials. DLC microelectrodes have been reported to commercial ELISA kits for detection of HIV antigen, HBV antigen and HCV antigen.

In the recent years, sensors research has become more materials oriented and the emphasis has been on advanced functional nano materials that serve as specific sensing layers. These novel materials include organic and polymer complexes and different oxides of Sn, Zn and Ba.

Synthesizing CP nanostructures with improved electrical conductivity and/or mobility will enhance the performance of the devices and many of the applications discussed. Several potential applications and corresponding challenges of these nanofibers and nanotubes in chemical, optical and bio-sensors, nano-diodes, field effect transistors, field emission and elec- trochromic displays, super-capacitors and energy storage, actuators, drug delivery, neural interfaces, and protein purification have been known.

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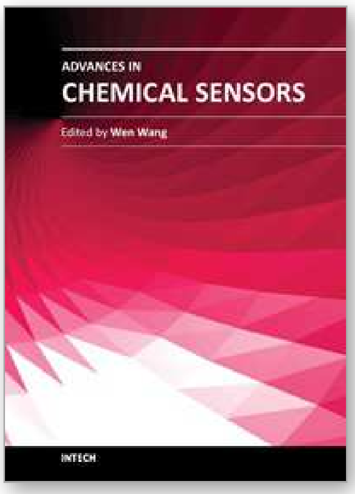

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The chemical sensor plays an essential role in the fields of environmental conservation and monitoring, disaster and disease prevention, and industrial analysis. A typical chemical sensor is a device that transforms chemical information in a selective and reversible way, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. Much research work has been performed to achieve a chemical sensor with such excellent qualities as quick response, low cost, small size, superior sensitivity, good reversibility and selectivity, and excellent detection limit. This book introduces the latest advances on chemical sensors. It consists of 15 chapters composed by the researchers active in the field of chemical sensors, and is divided into 5 sections according to the classification following the principles of signal transducer. This collection of up-to-date information and the latest research progress on chemical sensor will provide valuable references and learning materials for all those working in the field of chemical sensors.

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