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The Present State of Amperometric Nanowire Sensors for Chemical and Biological Detection

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Sensors and Electron Devices Directorate, ARL

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14. ABSTRACT

This report reviews the research in chemical sensing at the nanometer scale using amperometric detection focusing on publications from January 2004 to September 2005. The devices discussed fall into two categories: chemresistors and chemFETs. In either configuration, the number of carriers available in the channel, and hence the device's transconductance, changes as a function of analyte exposure. Devices based on inorganic nanowires (specifically limited to metal oxides and silicon), conductive organic polymer fibers, and carbon nanotubes are discussed as issues of sensitivity, selectivity, response/refresh times, etc.

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1. Introduction

Ultra-miniaturized autonomous sensors that can communicate the presence of chemical or biological agents in real time provide many strategic advantages to the Army. Examples of battlefield applications include the detection of airborne chemical attacks using UAV- or Soldier-mounted sensors to enable the evacuation of personnel or the activation of protective apparel before lethal doses are reached, and the identification of foodborne pathogens in shipments of rations to ensure a safe food supply and improve food transport efficiency (*1*). The goals in the development of such sensors include high sensitivity to one or more analytes of interest, and the ability to sense each analyte discretely against a complex background environment. For example, they must "be capable of distinguishing and rejecting common battlespace and environmental constituents (smoke, dust, pollen, ash, rain, sand, snow, etc.)" (*2*). An example of typical sensor specifications provided by the Joint Science and Technology Office for Chemical and Biological Defense is given in table 1. Sensors for both biological and chemical agents are expected to exhibit a 99% probability of detection, with 97% detection specificity.

The sensor system, including the sensing element, processor, communications circuit, and power source, must additionally be lightweight, small, and power efficient. The sensor could be attached to an unobtrusive location on the Soldier or supplies. For example, sensors could be incorporated into the fibers of clothing or packaging, and a Soldier would be unaware of the presence of the sensors unless they activate and signal a warning. Sensors have also been envisioned which use bio/electronic interfaces for the detection of biological processes or unknown, novel biological agents. Accordingly, a size scale of $(100\ \mu m)^3$ or smaller may ultimately be envisioned for the sensor subsystem, presenting specific scientific and technological challenges. For example, since chemical detection initiates with an absorptive or bonding chemical interaction mechanism, and the degree of chemical interaction scales with surface area, a large surface area in a small volume is desired to enhance the detected signal. The sensors must also consume small amounts of power to alleviate the weight load and maintenance associated with power source requirements. Some level of signal processing at the point of detection is required to filter the desired actionable information, and that information must be communicated to the next stage of action. Finally, the integrated system must be robust, and perform with near-zero false-positive rates under a wide range of temperature, humidity, atmospheric pressures, and mechanical stresses.

Materials and active devices which have been engineered at the nanometer length scale show promise in addressing these requirements. In addition to achieving extreme device miniaturization, nanowire and nanotube electronic materials are being extensively studied because the alteration of material properties at the nanometer size scale can have a large impact on their ability to react with the environment around them. Electrical, mechanical, thermal and other properties are changed relative to bulk material properties due to physical differences in the nanoscale entity. These include a relative prevalence of surface states, exclusion of dislocations, and phonon confinement and/or scattering. Physisorption of polar molecules, chemisorption of molecules, or changes in ion distributions at the surface alter the conductivity of nanowires by producing a local electric field which alters the nearby concentration of carriers in the wire.

Table 1. Point exposure sensing requirements for selected chemicals.

Chemical Agent	**Point exposure**
Nerve (VX)	$0.04\ mg/m^3$ in ≤ 90s
	$0.1\ mg/m^3$ in ≤ 30s
	$1.0\ mg/m^3$ in ≤ 10s
Nerve (GA, GB, GD, GF)	$0.1\ mg/m^3$ in ≤ 30s
	$1.0\ mg/m^3$ in ≤ 10s
Blister (HD, L, HN3)	$2.0\ mg/m^3$ in ≤ 120s
	$50.0\ mg/m^3$ in ≤ 10s
Blood (AC)	$22\ mg/m^3$ in ≤ 60s
	$2500\ mg/m^3$ in ≤ 10s
Blood (CK)	$20\ mg/m^3$ in ≤ 60s
Toxic Industrial Chemical (TIC)/ Toxic Industrial Material (TIM)	**Point exposure**
Ammonia (NH_3)	150 ppm
Arsine (AsH_3)	3 ppm
Carbon disulfide (CS_2)	550 ppm
Chlorine (Cl_2)	15 ppm
Diborane (B_2H_6)	20 ppm
Fluorine (F_2)	5 ppm
Hydrogen bromide (HBr)	20 ppm
Hydrogen cyanide (HCN)	50 ppm
Hydrogen fluoride (HF)	25 ppm
Nitric acid (HNO_3)	50 ppm
Phosgene (CCl_2O)	1 ppm
Phosphorous trichloride (PCl_3)	25 ppm
Sulfur dioxide (SO_2)	200 ppm
Sulphuric acid (H_2SO_4)	40 ppm

Chemical agent acronym key, with information taken from the websites http://www.cbwinfo.com/Chemical/CWList.shtml and http://www.chemindustry.com/apps/chemicals :
VX: Phosphonothioic acid; methyl-, *S*-[2-[bis(1-methylethyl)amino]ethyl] *O*-ethyl ester; $C_{11}H_{26}NO_2PS$
GA: Tabun – Phosphoramidocyanidic acid; dimethyl-, ethyl ester; $C_5H_{11}N_2O_2P$
GB: Sarin – Phosphonofluoridic acid, methyl-, 1-methylethyl ester; $C_4H_{10}FO_2P$
GD: Soman – Phosphonofluoridic acid, methyl-, 1,2,2-trimethylpropyl ester; $C_7H_{16}FO_2P$
GF: Cyclosarin – Phosphonofluoridic acid, methyl-, cyclohexyl ester, $C_7H_{14}FO_2P$
HD: Distilled mustard gas; 1-chloro-2-(2-chloroethylsulfanyl)ethane; $C_4H_8Cl_2S$
L: Lewisite, dichloro-(2-chloroethenyl)arsane; $C_2H_2AsCl_3$
HN3: nitrogen mustard 3,
AC: hydrogen cyanide, HCN
CK: cyanogen chloride, CClN

Since the Debye screening length is similar to the nanowire diameter, it is possible to achieve very sensitive conductivity response to induced polarization, with smaller wires being more sensitive. Nanostructured chemical sensors offer specific advantages due to large surface area to volume ratios which may result in increased sensitivity and reduced response times. In addition, active nanoelectronic sensor devices offer the promise of low power consumption and integration with supporting signal processing and communications electronics. While optical sensing approaches have shown promise in the areas of detection resolution and selectivity, those techniques are currently incompatible with chip integration. The ability to integrate sensors with existing and future signal processing and communication technologies is critical for a real-time battlefield sensor. Amperometric sensors allow electrical read-out which is simpler, both in hardware and in the avoidance of labeling requirements (e.g., fluorescent tagging), relative to optoelectronic approaches (*3*). Research activity in the area of nanoelectronic sensors has increased dramatically in recent years, as evidenced by the results of a Web of Science literature search of papers published by year for the period of 1990-2005, using the keywords “electronic nose,” “nanosensor*,” and “nanoelectronic*”, shown in figure 1.

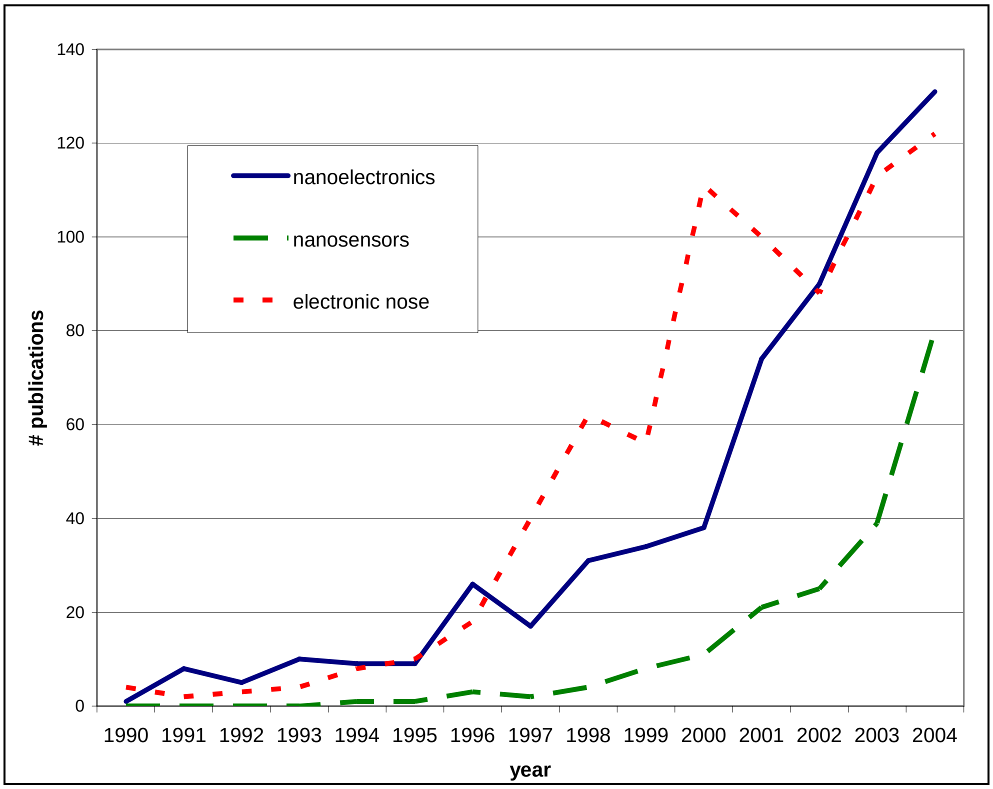

Figure 1. Web of Science literature search, by year for the period of 1990-2005, using the keywords “electronic nose,” “nanosensor*,” and “nanoelectronic*”. The period of January 2004 to September 2005 is analyzed in the current report.

This report reviews and summarizes the state of current research in chemical sensing at the nanometer scale through transport interrogation, defined as the monitoring of a given transport property to determine the presence of a chemical analyte. Accordingly, this report focuses on publications during the period of January 2004 to September 2005, with earlier published work discussed where appropriate. The main nanoelectronic device technologies addressed in this report are inorganic sensing devices (specifically limited to metal oxides and silicon), conductive organic polymer sensing devices, and devices based on carbon nanotube technology. Transport interrogation could include monitoring current through a device under conditions of constant bias, or monitoring a change in voltage under conditions of constant current. Although many of the interrogation techniques published to date and discussed in this report are direct current (DC) approaches, no restriction on specific detection technique should be implied. The transport interrogation devices discussed in this report fall primarily into one of two categories: chemresistors and chemFETs (for a general review see Gerard et al. (*4*)). The chemresistor (also called chemoresistor or chemiresistor) is the simplest possible chemical sensor. It is comprised of an element (such as a nanotube, polymer fiber, etc.) with a resistivity that is a function of analyte exposure. A chemFET is a field effect transistor (FET) structure which has either a chemically sensitive channel, or a chemically sensitive gate dielectric. In either configuration, the number of carriers available in the channel, and hence the transconductance, changes as a function of analyte exposure. Typically chemFETs are more sensitive devices, however, they may consume more power and are in general more difficult to fabricate than chemresistors. One distinct advantage of the chemFET is that in several cases the ability to actively reset the sensor has been demonstrated by simply reversing the gate bias. This is in contrast to most chemresistor examples which are either one time use only, or may have refresh times on the order of tens of minutes to hours.

In this report, the state of the art, in both the science and the technology, of nanoelectronic sensing devices will be addressed.

2. Inorganic Sensors

2.1 Metal Oxides

2.1.1 Introduction

Considerable effort is being put into the development of semiconducting metal oxide sensors. Tin oxide and zinc oxide are the two most commonly used materials. They are wide bandgap semiconductors, with bandgaps of 3.6 and 3.4 eV, respectively. While most commercial thin film or bulk metal oxide gas sensors are based on tin oxide (*5*), zinc oxide exhibits the widest variety of nanostructures, and possesses the additional features of being piezoelectric and biocompatible (*6*). Since tin oxide and zinc oxide are the most studied systems, they will be used as examples to illustrate the properties of metal oxide nanowires and devices.

2.1.2 Metal Oxide Nanowire Growth

A wide variety of growth methods have been used in producing metal oxide nanowires and other structures. Chemical vapor deposition in a tube furnace is the most widely used technique, where the growth is generally agreed to proceed via the vapor liquid solid (VLS) growth mechanism. In VLS growth, ZnO vapor is produced by heating a ZnO charge in the furnace, and adsorbs on a catalyst droplet which has a higher sticking coefficient. This droplet becomes supersaturated and precipitates the ZnO on the end of the growing nanowire (*7*).

The nanowire morphology is greatly influenced by the deposition conditions such as temperature, pressure, carrier gas, and substrate. A surprisingly large number of ZnO morphologies are attainable with these variables, including: nanowires, nanobelts, nanocombs, nanosaws, nanosprings, nanobows, nanopropellers, porous nanowires, (*8*, *9*) box beams, square nanotubes (*10*), etc. In all of these cases, the nanostructures are single crystalline with a preferred crystalline orientation. In the following discussion, the term nanowire will be used broadly to include some or all of the structures listed above.

Some other growth techniques which have been used to make metal oxide nanowires include molecular beam epitaxy, electrochemical deposition, pyrolysis, selective deposition, chemical etching, laser ablation, focused ion beam (FIB), x-ray/deep UV lithography, and melt injection into anodized aluminum pores (*6*-*8*, *11*-*18*).

2.1.3 Carrier Transport

Tin oxide and zinc oxide are both n-type semiconductors in which oxygen vacancies act as electron donors. As a result, the conductivity of the nanowires can be tuned by adjusting the density of oxygen vacancies. This is done by annealing the nanowires in various ambients. For instance, as-grown SnO_2 wires are typically non-conducting. Annealing at 800 ºC for 2 hours in 1 atmosphere of oxygen produces considerable conductivity. Subsequent annealing in vacuum, oxygen, or air can be used to tune the conductivity to the desired value. In fact, exposure to vacuum at room temperature can alter the conductivity by changing the amount of adsorbed oxygen species. Reducing the oxygen species in this way results in an increase in conductivity, while low temperature anneals in oxygen or air does the reverse (*7*).

In addition to carrier donation by oxygen vacancies, the wires may be doped by atomic substitution such as Mg implantation into ZnO (*6*). Carriers have also been donated to a nanowire from smaller bandgap nanoparticles on the surface, as demonstrated for CdS on ZnO nanowires (*19*). The conduction mechanism has been determined to be variable range hopping for ZnO (*20*) and vanadium pentoxide (*21*). Electron mobilities in ZnO have been reported in the range of 17 to 200 cm^2/Vs (*5*, *15*). Other reported electron mobilities include: 160 cm^2/Vs for tin oxide, 100 cm^2/Vs for indium oxide, 10 cm^2/Vs for tungsten oxide, and 0.4 cm^2/Vs for titanium oxide. Ni oxide, which is a p-type semiconductor, is reported to have a hole mobility of 0.2 cm^2/Vs (*5*). Conductivities spanning 0.09-75 $\Omega^{-1}cm^{-1}$ have been reported for ZnO. The electron diffusion length has been measured to be on the order of 1-5 nm, so that the nanowire is still effectively 3D as far as the electron is concerned (*20*, *22*). 3D transport is further supported by the observation of negative differential resistance regime. It has been proposed that this results from carrier redistribution to the wire surface, with increasing source-drain bias, where the mobility is reduced due to scattering (*17*).

2.1.4 Detection Mechanisms

Physisorption of polar molecules, chemisorption of molecules, or changes in ion distributions at the surface alter the conductivity of nanowires by producing a local electric field which alters the nearby concentration of carriers in the wire. Since the Debye screening length (the depth the field will penetrate into the material) is similar to the nanowire diameter, it is possible to achieve very sensitive conductivity response to induced polarization (*23*) due to a shifting of the Fermi level away from the conduction band throughout the wire (*17*). Adsorption of electron donating species, such as NH_3, will increase conductivity while electron withdrawing groups, such as NO_2, will reduce conductivity. In fact, the detected species may produce a response by merely interacting with adsorbed species such as O_2^{2-}, O^-, O^{2-}, H^+, or OH^-, (5, *6*). For instance, ethanol reacts with O^- releasing electrons back into the wire which is then more conductive (*24*).

The correlation between the Debye length and the nanowire diameter is the basis of the increased sensitivity of nanowire sensors as compared to bulk or thin film sensors. In the nanowires, the carrier concentration is altered thoughout the entire wire, whereas for macro sensors, the conductivity is only affected near the grain boundaries (*25*). Comparing nanowires to thin films of similar thicknesses, the nanowires experience a square root of three more depletion since there are fewer charges available as the depth of penetration increases (*11*). As nanowires get smaller, they become more sensitive. A surface potential will change the conductance of a 50 nm wire 20 times more than for a 200 nm wire (*3*).

2.1.5 Sensor Devices

Metal oxide sensing elements are well suited to either of the two basic types of sensors described earlier. Chemresistors may be a single or multiple wire device. The multiple wire devices may comprise many wires in parallel (*11*) or may be made using a mat or paste of nanowires. Metal oxide chemresistors may be operated at room temperature, or they may be operated at elevated temperature (e.g., 200-400 °C). For example, a paste chemresistor uses a nanowire paste applied between gold electrodes on an alumina rod which contains a heating element (*26*). The reported resistance of one such sensor is in the GΩ range (*24*). Sensor response times in the tens of seconds and recovery times in the tens of minutes have been reported for bulk and thin film sensors (*5*). It is anticipated that nano-sensors could improve these speeds. A ten minute response time has been reported for a titania nanowire chemresistor detecting hydrogen (*16*), while a ~30 second response time has been reported for a multi(nano)wire carbon monoxide sensor (*17*). A single gallium oxide nanowire ethanol sensor with a 2.5 second response time has also been reported (*27*).

ChemFET structures are most commonly fabricated using the nanowire as the channel and the supporting substrate as the gate (*15*, *17*, *22*, *28-30*). The substrate is typically a conductive wafer serving as the gate, with a surface oxide to prevent electrical shorting of the gate to the wire. Using this backside gating approach, the carrier concentration is changed along the entire length of the nanowire and not just in a localized region as would be the case with a localized gate electrode. The advantage of using a gate electrode is that by electronically adjusting the carrier concentration in the wire, the sensitivity of the sensor can be adjusted, and as will be discussed later, there is the potential of tuning the selectivity as well (*17*, *22*). Switching ratios of 100 (*6*), 1000 (*22*) and even up to one million (*31*) have been reported. An indium oxide multiple nanowire chemFET sensor for ammonia has exhibited a ~1000 s response time.

While single wire and multiple wire devices have been demonstrated, the most desirable approach has not yet been determined. Single wire devices promise the fastest speeds and lowest power consumption, while holding the potential for single molecule detection (*29*). On the other hand, multiple wire devices will likely be more reliable, easier to fabricate, and they will average out the variations in response of individual wires (*30*). They may have an additional contribution to sensitivity from nanowire/nanowire junctions which, upon adsorption of the analyte, reduce conductivity by more than the surface depletion (*30*). However, multiple wire FETs will exhibit reduced gate sensitivity if the wires are stacked such that some of them are separated from the gate (*30*).

2.1.6 Analytes/Sensitivity/Reversibility

The analytes which have been detected by metal oxide sensors are typically oxidizing or reducing species. Demonstrated sensor applications have included: acidity (pH), hydrogen (H_2), humidity (H_2O), propane (C_3H_8), hydrogen sulfide (H_2S), methanethiol (CH_3SH), ethanol (C_2H_5OH), liquefied petroleum gas (LPG), nitric oxide (NO), nitrous oxide (NO_2), acetone (CH_3COCH_3), $C_5H_{11}CHO$, carbon monoxide (CO), ammonia (NH_3), $(CH_3)_3N$, ozone (O_3), methane (CH_4), $CH_3COC_2H_5$, $(C_2H_5)_3N$, C_2H_2, and CH_3SSCH_3 , butane and acetylene among others (*5*, *26*). Detection limits have been reported for various species: 200 ppb NO_2 (23), <1 ppm ethanol vapor (*25*), and 2 micromolar H_2O_2 (32). It has been suggested that single molecule detection may be possible (*29*). A pH sensor with a linear pH response over the range 2-12 and 0.1 pH resolution has also been reported (*33*), and device design may improve sensitivity. For instance, the frequency of a ring oscillator changes by more than the mobility of one of its component FETs (*29*).

While the liquid sensors typically operate at room temperature, the gas sensors have a range of operating temperatures, usually from room temperature up to about 400 ^{o}C. The elevated temperatures sometimes used with chemresistors help increase reaction rates and sensitivity as well as producing reversible binding/reaction, although too high a temperature can prevent adsorption of the analyte (*5*). UV irradiation, with energy of more than the bandgap, can also be used to reset the sensor by desorbing the bound species and releasing charge trapped at the interfaces which causes hysteresis (*5*, *17*, *30*). Another method of refreshing the sensor demonstrated in chemFETs is to apply a strong gate pulse which was shown to electrodesorb NO_2 and NH_3 adsorbates. In particular, a pulse of –30 V/60 seconds was enough to drive off NH_3 while –60 V/60 seconds was required to drive off NO_2 (*23*).

2.1.7 Selectivity

Metal oxide sensors are lacking in selectivity, as most adsorbed species will produce a depletion layer, and any interaction with surface complexes such as O^-, O_2^-, H^+, or OH^- will produce a response (*6*), as will any Lewis acid or base. Indeed, the multiple reaction pathways in which one analyte may participate may produce another type of selectivity problem, since the multiple reactions may complicate the calculation of surface concentration from the measured conductance (*17*). Due to the poor selectivity of simple devices, most of the sensors reported have been tested using a model system such as ultrapure water or Ar gas containing a dilute amount of the analyte of interest. Some of the gas sensing demonstrations used room air including humidity. However, many approaches to improving selectivity using chemical, physical, electronic, or pattern recognition means have been proposed.

Chemically, the nanowires could be modified by including additives, catalysts, promoters, or surface functionalization to improve the selectivity or greatly increase the sensitivity to one component of the mixture to be analyzed (*5*, *33*). Some common chemistries for functionalizing metal oxides include the use of carboxylic acids, phosphonates, siloxanes, or hydroxamic acids (*12*). An approach similar to functionalization, which could be applied to chemFETs, would be to use chemically sensitive gate dielectrics (perhaps coupled with an enzyme, e.g., glucose oxidase, which reacts specifically with the analyte of interest) (*29*).

Selectivity based on physical properties could include adsorption selectivity as a function of temperature (*5*) and size exclusion or other separation using nanotubes (*12*). A selective separation step might also be performed by a permeable coating on the sensor (*30*). A process for plasma polymerizing polypyrrole on to Au nanowires has already been demonstrated (*34*). An electrically conductive nanoparticle or nanowire composite using a nonconductive matrix, which swells by selectively absorbing the analyte, has also been suggested as a potentially viable sensor concept (*29*).

The ability to electronically change the selectivity of the sensor may be the most interesting approach. It has been demonstrated that two different analytes, NH_3 and NO_2, required different bias pulses to desorb them from the sensor (*23*). A related approach would use changes in the carrier concentration to affect surface chemical properties and reaction rates by changing the number/potential energy of electrons available to participate in the reactions. The carrier concentration could be changed by doping (*5*, *24*, *27*) or with the applied gate bias (*17*, *22*). A type of selectivity based on differences in doping has already been reported. A multiple wire device with individual wires having varying amounts of oxygen vacancies had individual wires which exhibited conductance changes in opposite directions upon adsorption of NH_3. The "ensemble averaging" resulted in insensitivity to NH_3 while maintaining sensitivity to and therefore selectivity for NO_2 (*30*).

The selectivity of some or all of the approaches above could be further multiplied by using pattern recognition and an array of different sensors (*28*, *29*). The variety of sensors could also include sensor elements with more complex compositions such as: heterostructure, junction, and barrier composite nanobelts; complex oxides with two or more types of cations; and/or multiple types of nanobelts which would have different responses to a given analyte (*7*).

2.1.8 Other Issues

There are a number of additional issues, such as reproducibility of fabrication, stability, contact effects, packaging convenience, power requirements, etc. (*29*) that will need to be addressed for this technology to be viable. Stability is an issue with metal oxide nanowires, since exposure to oxidizing or reducing environments can change the degree of doping of the wires so that there may be memory effects from the order of measurements or processing steps. Some of these surface oxygen vacancies can diffuse into the bulk of the wire where they are less susceptible to surface chemistry and can result in long term stability issues. Trapped charges may produce hysteresis effects. Adsorbed contaminants or substrate impurities may also affect reproducibility and reliability. Some of these problems may be minimized with appropriate measurement protocols, cleaning routines, and heat or UV light irradiation (*17*). On the other hand, nanowires may provide some advantages over thin film or bulk sensors. Since nanowires are usually high quality single crystals, there will be no sensor drift from Oswald ripening as there can be in polycrystalline sensors (*5*, *7*).

Integration of nanowires into circuits presents another significant challenge. There is a need to align, self-assemble or selectively grow these nanowires so that they may be integrated into devices (*7*). Different materials and growth methods will undoubtedly require different solutions. While pick and place methods may be useful for prototyping individual sensors, massively parallel methods of aligning nanowires will be required to make large numbers of sensors economically. Large sensor arrays will have the additional requirement of aligning (and addressing) large numbers of dissimilar nanowires.

2.1.9 Conclusions

A wide variety of growth methods have been used to produce metal oxide nanowires, which are typically n-type semiconductors in which oxygen vacancies act as electron donors. The conductivity of these nanowires can be tuned by changing the density of oxygen vacancies, but this can also result in undesirable memory effects due to exposure to oxidizing or reducing environments. The analytes, which have been detected by metal oxide sensors, are typically oxidizing or reducing species with detection limits in the ppm and sub-ppm range. In fact, the detected species may produce a response by merely interacting with other adsorbed species. As a result, very little selectivity has been demonstrated to date. However, many approaches to improving selectivity/sensitivity using chemical, physical, or electronic means have been proposed. Chemically, the nanowires could be modified by including additives, catalysts, promoters, or surface functionalization to improve the selectivity or greatly increase the sensitivity to one component of the mixture to be analyzed. A selective separation step might also be performed. The ability to electronically change the selectivity of the sensor may be the most interesting approach.

2.2 Silicon

2.2.1 Introduction

While silicon nanowire sensors are in many ways similar to the semiconducting metal oxide sensors described above, there are some interesting differences or additional information that warrant further discussion.

2.2.2 Si Nanowire Fabrication

Two approaches to Si nanowire fabrication have been used. Bottom-up fabrication using CVD in a furnace with silane precursor gas and metal nanoparticle catalysts has been used, with both n- and p-type nanowires demonstrated (*11*, *35-38*). In fact, CVD has been used to grow carbon nanotubes on top of Si nanowires to produce heterostructures (*39*) and to produce SiC nanowires (*40*). One innovative metal catalyzed CVD approach uses the fact that the nanowires preferentially grow perpendicular to a Si [111] face to produce aligned nanowires that grow across a trench in a Si substrate. The trench sidewalls are heavily doped to provide electrical contacts (*11*).

The top-down fabrication approach eliminates some of the alignment, assembly, and feature pitch issues associated with most bottom-up approaches. Top-down fabrication has been achieved using conventional Si IC processing. For example, e-beam lithography and reactive-ion etching (RIE) has been used to produce Si nanowires (supported by oxide) using Si-on-insulator (SOI) wafers (*3*). A more elaborate approach referred to as the SNAP process, uses a selectively etched (Al)GaAs superlattice to produce a ridged template which is then metalized. The metal is then transferred to an SOI wafer using epoxy and a (Al)GaAs etch. These metal nanowires are then used as a shadow mask for subsequent plasma ashing (epoxy) and reactive-ion etching (Si) steps to produce closely spaced and aligned Si nanowires (*41*).

Mechanically there are limits as to what can be fabricated. It has been calculated that a 10 nm Si nanowire will collapse under its own weight at a length of 40 microns, and a 100 nm Si nanowire will collapse at 800 microns long (*11*).

2.2.3 Carrier Transport

A dopant concentration in the mid 10^{19} cm^{-3} has been proposed as the maximum allowing complete carrier depletion (*11*). It should be noted that there may be limits to the doping of very thin nanowires. Concern has been expressed that doping very thin wires (a few nm in diameter) might result in dopant atoms segregating to the surface or being of such low numbers that a fluctuating potential might be created which would impede current flow (*11*). Defects also become more of an issue as nanowire size decreases. As a result, the doping method is important, with MBE doping being the best and ion implantation the worst. Wires made from implanted Si were highly conducting down to about 50 nm, but below that, the wires were routinely resistive as the implantation defects limited the conduction. Processing may induce conductivity limiting defects as well. Spin-on glass doped wafers produced small wires with better conductivity (still >1 TΩ) compared to implanted wafers, but the wires were still about ten times worse than those from MBE wafers. The wires produced from MBE doped material had conductivities comparable to the bulk material. Clearly, choice of starting materials, doping method, and etching procedures are important for producing conductive nanowires below 50 nm (*41*). SiC nanowire substrate-backgated FETs with a resistivity of 2.2×10^{-2} Ωcm and a mobility of 15 $cm^2V^{-1}s^{-1}$, have been reported. The low mobility was ascribed to a high carrier concentration and high trap density due to a poor quality gate oxide (interface scattering) (*40*).

2.2.4 Detection Mechanisms

The detection mechanisms are essentially the same as described for the metal oxide nanowires above in so far as changes in ion distributions at the surface or surface binding events can alter the conductivity of the nanowires by producing a local electric field which alters the nearby concentration of carriers. While Si nanowires have been functionalized with binding sites for small molecules providing analyses similar to metal oxide sensors, they have also been demonstrated with binding sites specific to large biomolecules and even viruses.

2.2.5 Sensor Devices

Both chemresistors and chemFETs have been demonstrated, as have gas and liquid phase sensors. Many of the biomolecule sensors use a microfluidic channel to deliver the analyte to the sensor. This channel can be formed by etching a trench in the substrate which is then sealed with a glass coverslip, or by applying a flexible polymer microchannel to the chip. Frequently, the microfluidic channel is also used during the functionalization of the nanowire, after it has been cleaned with various gases, liquids and plasmas (*36*). After functionalization, the remaining non-active surface sites are passivated. Polyethylene glycol is used to prevent nonspecific binding to the channel. A surface DNA probe coverage of 3E15 μm^{-2} has been reported which agrees well with the 3.3 nm^2 footprint of the 12-mer probe used (*42*).

2.2.6 Analytes/Sensitivity/Reversibility

Analytes detected have included pH, ionic concentration, gas phase ammonia, and gas phase water (*29*). Biological applications include the detection of oligonucleotides/single stranded DNA (*3*, *42*), a specifically mutated (cystic fibrosis) gene (*35*), viruses (*36*), and molecules of biochemical significance such as adenosine triphosphate (ATP) (*37*). Complementary single-strand DNA/oligonucleotides or peptide nucleic acids have been used for binding DNA/oligonucleotides (*3*, *35*, *42*). Antibodies and binding proteins have been used for viruses (*36*) and ATP (*37*), respectively.

Good sensitivities have been achieved. 12-mer oligonucleotides have been detected with < 10 pM sensitivity (*3*, *42*), while DNA has been detected at 10's of fM (*35*). Viruses such as influenza type A, avian adenovirus group III and avian paramyxovirus have been detected at 10^{10} –10^{11} particles/ml with reversible binding on a 20 second to >10 minute time scale (*36*). ATP has been reversibly detected at concentrations at least as low as 100 pM using an Abl protein probe (*37*).

2.2.7 Selectivity

Selectivity using the biological probes appears to be excellent. For instance, a 1000 times higher 12-mer oligonucleotide concentration with a one base pair mismatch only produced a weak signal due to nonspecific binding (*3*). The time constant of the reversibility of the detector response is also a measure of the binding kinetics and can be used to distinguish between specific and nonspecific binding (*35*). However, some prepurification may still be advisable. For instance, the charge-based DNA detection sensitivity is improved by reducing the ionic concentration of the fluid, which reduces the counter-ion screening of the DNA negative charge (*42*). Virus detection was very selective with structurally similar viruses being discriminated by the antibody receptors. While short-duration conduction changes occurred due to random contact between unspecific viruses and the nanowire, the targeted virus could be identified by the duration of the conductivity changes which is related to the virus/antibody binding and unbinding kinetics (*36*). In the case of ATP sensing, it was demonstrated that competitive inhibitors could reduce the response of the sensor to ATP. An inhibitor such as Gleevec can do so without inducing much of a signal itself as it is uncharged, while ATP is negatively charged (*37*).

2.2.8 Conclusions

Both bottom-up and top-down fabrication of n- and p-type Si nanowire sensors has been demonstrated. The conventional top-down IC fabrication approach eliminates some of the alignment, assembly, and feature pitch issues associated with most bottom-up approaches. Both chemresistors and chemFETs have been demonstrated, as have gas and liquid phase sensors. The liquid phase sensors frequently incorporate a microfluidic channel to deliver the analyte. While the Si nanowire detection mechanism is essentially the same as described for the metal oxide nanowires above, improved selectivity has been demonstrated with Si nanowires that have been functionalized with binding sites for small molecules, large biomolecules (e.g., single stranded DNA), and even viruses. Good sensitivities have been achieved with 12-mer oligonucleotides being detected with <10 pM sensitivity, while DNA has been detected at 10's of fM. Specific viruses have been detected at 10^{10}-10^{11} particles/ml. While selectivity using the biological probes appears to be excellent, some prepurification may still be advisable. For instance, sensitivity is improved by reducing the ionic concentration of the fluid, which reduces the counter-ion screening of the analyte's charge. Prepurification could also reduce competitive inhibitors for the sensor binding sites.

3. Organic Sensors

3.1 Conducting Polymer Sensors

3.1.1 Introduction

The ability to functionalize polymers is a powerful tool for creating materials which are sensitive to specific chemical or biological environments (CBE). The final goal of any sensor development is to produce a device which shows a signal response to changing CBE. In the case of conducting polymers, it is desirable to incorporate a polymer–functional group combination into a resistive element whose value changes in a predictable fashion as a function of the concentration of a particular chemical of interest (COI).

As with metal oxide devices, both chemresistors and chemFETs have been demonstrated. However, despite the fact that devices have been fabricated which show a resistance response to a COI, considerable research in this area remains to be done to realize functional sensor platforms. In particular, an improved understanding of the metal-polymer contact is required, polymer and functional group combinations must be designed to optimize chemical specificity, and theoretical limits to the achievable sensitivity of these devices must be determined.

3.1.2 Frequently Used Polymers

Since there is an extensive list of polymer types and functional groups, a nearly infinite number of combinations of the two could ultimately be used for detecting a specific COI. This section will attempt to summarize the types of polymers which appear more frequently than others in the literature.

Polyanaline has been functionalized to be sensitive to biological agents such as hemoglobin, lipids, uric acid, and tryglicerides (*4*). This polymer can also be electrospun into fibers with diameters as small as 15 nm (*43*). The literature suggests that polyanaline shows potential as a single polymer device solution, in contrast to systems where insulating fibers are coated with films of conducting polymers. One problem with polyanaline fibers is that oxidation effects will change electrical properties over time (*43*).

Polypyrrole is another polymer which has been successfully functionalized for detection of cholesterol, glucose, fructose, and urea, among other analytes (*4*). However, very little is available in the literature about the transport properties of this polymer, and there has been no evidence that it has been spun into nano-fibers. However, Covington et al., have shown polypyrrole based chemFET response to organic vapors (*44*), indicating that there is a precedent for electrical response to a chemical environment.

Although oligothiophene appears in only a handful of references, these papers have much more detailed data about the performance of actual sensor devices. The work by Crone et al., (*45*, *46*) shows transport response in different types of oligothiophene chemFETs to pentanol, butanol and nonanol. Their conclusions, based upon the detection of these simple alcohols, is that the longer the functional end group on the conducting polymers, the greater the transport response to a particular COI.

Very little information on carrier transport measurements in conducting polymer films as a function of chemical exposure was found in the literature. Much more is published regarding optical measurement or isotope tracing measurements of chemical adsorption, but no link between optical response and transport response is suggested. The papers by Crone and co-workers are an exception, and provide a useful experimental model for testing the utility of transport based chemical detectors. Plots of time-dependent current or resistance correlated with the introduction of controlled chemical environments are available in their reports (*45*, *46*).

3.1.3 Detection Mechanisms

The voltage response under conditions of constant current, or the current response under constant bias of a particular device are both related to resistance and its reciprocal, conductance. That is why the term ‘transport properties’ has been used rather generally to include all categories of electrically probing the conducting polymers. The detection of changing transport properties in a particular device is related to the details of the entire sense circuit which is ultimately used to convert the device response to a signal which can be processed.

Of scientific interest are the mechanisms which cause this change in transport properties. Conceptually, there are two effects which can alter transport properties in a film. The first is by simply altering the number of carriers. When an analyte is absorbed by the conducting polymer, the chemical bond between the analyte and the polymer site re-organizes the electron configuration in both, and results in a localized change in the amount of carriers available. Depending on the details of the reaction, there could either be more carriers, or less, as proposed by Covington et al., (*47*) to explain the response of carbon black composite polymers to chemical vapors.

However, Covington and co-workers could not eliminate a second possible mechanism which is due to a mechanical change in the polymer film. In this case, the absorbed analyte creates a swelling in the polymer. Since transport through conducting polymers is due to wave function overlap (*48*), changes in the intermolecular spacing can have a measurable impact on transport. In fact, Torsi et al., were able to correlate the adsorption of pentanol on α,ω-dihexyl-α-quarterthiophene with both an increase in film resistance and a morphological change (*49*). In this case, the swelling distorted the grain boundaries enough to disrupt transport.

It is certainly conceivable that swelling could have the opposite effect, namely closing gaps in a film and therefore increasing orbital overlap between molecules of separate grains. In fact, Covington et al., report both increased and decreased resistance as a function of polypyrrole exposure to toluene and ethanol, respectively (*44*). However, without corresponding morphology data, it is not possible to eliminate one of the two possible mechanisms.

For sensor device engineering, it will be important to understand the two dominant mechanisms relative to the measured response of conducting polymers to analytes. Experiments designed to distinctly identify the relevant mechanisms need to include both transport and morphology measurements.

3.1.4 Metal-Polymer Contacts

While the development of polymers and functionalization groups is typically the domain of chemists, the injection of carriers into conducting polymers for the development of electronic circuits is still challenging. A review paper by Scott (*50*) gives a detailed description of the physics involved in charge injection into an organic film, emphasizing the challenging fact that there is not a well defined Fermi level in the organic. Additionally, it is unclear if the vacuum levels align at the surfaces creating a Mott–Schottky interface. Therefore, the charge injection is not simply tunneling through a potential, nor does it follow a simple thermionic emission model. Rather it is a hybrid process. There is experimental work in the literature which suggests that some metal-organic contacts might be better than others. For example, Hosseini et al., have achieved ohmic contacts from Pt on MDP,N,N,N',N'-tetra-p-toly-4-4'-biphenyldiamine. The ohmic nature of the contact was confirmed both by transport measurements and Kelvin probe measurements (*51*). Chromium was also used in the study, but did not yield an ohmic contact.

Gold is used as a contact metal in the overwhelming majority of the papers which employ a metal–polymer contact, due to the stability of the gold and its resistance to oxidation. However, this property may result in the typically observed high contact resistance between the gold contacts and the polymer. Certainly the better the chemical adhesion is between the two materials, the better the electron state overlap should be and hence the better the contact. An improved understanding of the nature of the metal–polymer contact is essential for the realization of a functional chemresistor sensor device.

3.1.5 Sensitivity and Selectivity

The published sensitivities vary widely in the literature. This is due in part to the specific device, the measurement method, and the ability to control the concentrations of analytes with which the devices are tested. While chemFETs are typically considered more sensitive than chemresistors, organic polymer chemresistors have been shown to be sensitive to several hundred ppb for ammonia (*52*). To put into context the level of detection that would be useful for Soldier-borne sensors, detecting VX nerve agents at a level of 5 ppm would give the Soldier about 45 min to clear the area before a lethal dose was reached (*53*). In the work by Joseph et al., (*52*) chemresistors made from Au and Pt nanoparticle doped 1,9-nonanedithiol were demonstrated to detect ammonia down to 300 ppb. However, those sensors were also sensitive to toluene, water, carbon monoxide and ammonia, making them very susceptible to false positive readings.

Selectivity is a critical element of chemical or biological sensor design. In most cases, chemresistors and chemFETs described in the literature have been shown to be sensitive to groups of chemicals. For example, Joseph et al., (*52*) discuss chemresistors sensitive to solvent vapors, while Torsi et al., (*46*) describe devices sensitive to alcohols. Polymers hold great promise in the detection of chemical species due to the vast potential for combination of polymers and functional groups that may be synthesized. Although high selectivity devices have not yet been demonstrated, strong precedent exists within the pharmaceutical industry for developing chemicals which are highly targeted. True selectivity may be accomplished not with a single device, but rather with an array of devices and proper signal processing. Much like the nose of a dog, these arrays may have a number of elements, each sensitive to groups of chemicals. By interrogating each of the elements of the array for a positive or negative response, the range of possible analytes causing the signal can be narrowed.

3.1.6 Reliability and Saturation

The reliability and robustness of a sensor is a critical consideration in the device performance. This is particularly important for deployment into the battlefield and operation in life-critical conditions. In the case of the chemresistor, the inherent simplicity of the device lends itself to being quite robust. Even the chemFETs are very simple by integrated circuit standards and could potentially withstand impact. Of primary concern is whether or not the actual detection mechanisms can become saturated through exposure, and if so, if it is possible to refresh them. Many examples exist for fabricated chemresistors as single-use sensors due to irreversible loading. However, there are also examples of chemresistors which refreshed on their own rather quickly (*54*). There is also precedent for devices that did not refresh automatically but could be refreshed electronically. In their detection of pentanol with chemFETs, Torsi et al., noted that the unassisted refresh rate of their devices was quite poor (*46*), taking nearly an hour for the films to refresh after the pentanol vapor was removed. However, by reverse biasing the gate, the chemFET could be refreshed immediately.

The response of each functionalized polymer and analyte combination must be investigated on a case by case basis. The precedent for both reversible and irreversible loading is important to keep in mind in the development of polymer-based sensor design, as is the demonstration of reversal of the loading process for sensors which do not automatically refresh.

3.1.7 Conclusions

While the literature reports of chemresistors or chemFETs based on electrical interrogation of polymer films or nanofibers is limited, the field is relatively young and the number of polymers and functional groups is extensive. Additionally, the electrical measurements reported for these materials are not exhaustive. While DC transport measurements on chemresistors present a simple approach, limitations of high metal–polymer contact resistance may present a limiting factor and warrant a more sophisticated approach to the investigation of polymer sensing elements. For example, the use of the polymer as the dielectric in a capacitor may yield a capacitance change with analyte concentration that may be more sensitive than a DC transport change. Alternatively, alternating current interrogation schemes may be a useful approach.

3.2 Carbon Nanotube Sensors

3.2.1 Introduction

Carbon nanotubes are interesting materials that have the potential to revolutionize electronics, with potential applications that range from field emitters to chemical and biological sensors. Their exceptional properties – extremely high mobility, small size, and high tensile strength – make them ideal 1-D conductors.

3.2.2 Structure

A carbon nanotube is made up of a single layer of graphite (called graphene) that rolls up on itself into a cylinder. Its structure, including tube diameter and chirality, and electronic properties are strongly dependent upon the lattice vectors along which the tube has folded. Depending upon this direction, the nanotube will exhibit either metallic or semiconducting behavior. A typical single wall carbon nanotube (SWNT) is 1.5 to 5 nm in diameter; however, SWNTs can be hundreds of microns or even centimeters long (*55*).

In many cases, a nanotube does not consist of one single layer of graphene. Instead, it can be composed of many graphene layers or walls and thereby named multiwall carbon nanotubes (MWNT). The diameter of MWNTs can range anywhere from 10 to 100 nm. The electronic properties of the nanotubes are also influenced by whether the tubes are single or multiwalled. Single wall tubes can be either metallic or semiconducting. MWNTs usually exhibit a combination of these two properties and therefore are usually considered metallic.

3.2.3 Growth

Carbon nanotubes can be grown by a variety of methods, including arc-discharge, laser ablation, high pressure CO process (HiPCO), and chemical vapor deposition (*55-57*). Despite the variety of these growth methods, the key to carbon nanotube growth lies with the use of a catalyst. The catalysts are small metal nanoparticles from which the carbon nanotubes nucleate. The diameter of the resulting nanotubes is determined by the diameter of the nanoparticles (*57*). Nickel and cobalt metals have been successfully used for seeding growth; however, the most widely used catalyst is iron. The iron catalyst particles are derived from many sources, including ferric nitrate ($Fe(NO_3)_3$ and ferrocene ($Fe(C_5H_5)_2$. There are two common methods of introducing the catalyst: supported or floating (*58*). Supported catalyst growth occurs when the catalyst is deposited on the substrate and then placed inside the growth vessel. Floating catalyst involves the delivery of the catalyst in the vapor phase into the growth chamber. Ferric nitrate is typically used as a supported catalyst and ferrocene as a floating one.

The most common growth method for carbon nanotubes is chemical vapor deposition (CVD) (*57*). For CVD of carbon nanotubes, carbon precursor gases (i.e., methane, ethylene, and/or acetylene) and hydrogen are reacted in a furnace at temperatures in excess of 500 °C. Typically, multiwall carbon nanotubes are deposited between 550 °C and 750 °C, whereas single wall nanotubes require higher temperatures to form, between 800 °C and 1000 °C. Moreover, plasma-enhanced chemical vapor deposition (PECVD) has been developed to enhance the growth of carbon nanotubes, in particular multiwall carbon nanotubes. Here, high energy electron impact is responsible for activating the gases, whereas thermal energy is used to activate the carbon precursor gases in traditional CVD growth (*58*). Vertically aligned carbon nanotubes are typically grown using this method.

Carbon nanotubes are typically grown in two different configurations - horizontal or vertical. The configuration largely depends upon the growth conditions. Horizontally directed carbon nanotubes are grown with the long direction of the nanotubes parallel to the substrate surface. These are typically deposited by CVD under constant flow at or near atmospheric pressure. Horizontal nanotubes can be either single wall or multiwall. Vertical nanotubes are grown under a variety of conditions. Typically, they result from conditions of low pressure or no flow. Vertical aligned nanotubes have their long tubal direction perpendicular to the substrate surface and are almost always multiwalled nanotubes.

Regardless of growth configuration, the exact growth mechanisms of the carbon nanotubes are still not fully understood. What is clear is that the catalyst plays a pivotal role in nanotube formation. The initial size of the nanotube is dictated by the size of the catalyst nanoparticle; therefore, it plays an important role in establishing whether the tube will be single- or multi-walled. The carbon nanotubes can either grow from the catalyst as the nanoparticle 1) remains attached to the substrate (base-type growth mode) or 2) detaches from the substrate and remains at the tip of the nanotube (tip-type growth mode) (*58*). Evidence for both methods has been observed. Recent work has shed light on how the catalyst aides the formation and development of carbon nanotubes. The catalytic reaction between methane and nickel nanoparticles at 500 °C was observed by high resolution transmission electron microscopy (*59*). It was observed that the catalyst particles moved with the growing nanotube, indicating that the point of growth occurs at the catalyst-tube interface. It was also found that the catalyst itself undergoes a shape transformation during growth. The shape transformations of the metal nanoparticle occurred in different stages as the catalyst itself became coated with a graphite layer from the decomposition of methane. This reshaping promoted the nucleation and growth of the graphene layers of the nanotubes (*58*). Note that, while this growth mechanism has been observed, it may only be valid in specific growth conditions and may not represent all carbon nanotube growth conditions.

3.2.4 Carrier Transport

The electronic properties of carbon nanotubes are strongly dependent upon their structure. Semiconducting single wall carbon nanotubes have a band gap of ~0.5 eV. The band gap of carbon nanotubes is inversely proportional to the tube diameter (*56*). They are typically p-type (or hole doped) due to the presence of adsorbed molecular oxygen on the surface (*55*, *56*). Semiconducting carbon nanotubes exhibit excellent transport properties, with measured mobilities as large as 79,000 cm^2/Vs (*60*). Metallic nanotubes are insensitive to gate voltages applied by an electrode. Small changes in the Fermi level do not significantly alter the conductance through the metallic tubes.

3.2.5 Detection Mechanisms

The detection mechanism for carbon nanotube based sensors is physisorption or chemisorption of atoms, molecules, and/or large chemical compounds onto the CNT surface. Upon adsorption, a change in the electrical conduction of the device is observed. Although the exact mechanism responsible for this conduction change is still unknown, there are two main mechanisms proposed to describe this phenomenon. The first possibility is that analyte adsorption on the nanotubes affects the dielectric constant of the carbon nanotubes (*61*, *62*). The conduction change arises in order to balance out the added/reduced charge of the device. The second proposed mechanism involves charge transfer from the adsorbed molecule to the nanotube which causes changes in the electrical conduction (*61*, *63*, *64*). Charge transfer is thought to occur either through direct interaction between the adsorbed analyte and the CNT or through electrostatic effects via an intermediary charged species on the CNT and/or surrounding substrate. The charge transfer mechanism is strongly dependent upon the chemical nature of the adsorbed species. This dependence is exemplified in the work by Kong et al., using p-type SWNT-based sensors to detect nitric oxide (NO_2) and ammonia (NH_3) gases (*64*). NO_2, a strong oxidizer, is believed to attract electrons from the carbon nanotubes, thus leaving more holes in the SWNTs for additional conduction. However, NH_3 is believed to either bind to the hydroxyl groups on the SiO_2 substrate or another species present, such as preadsorbed oxygen on the CNTs, which can partially neutralize the charge transfer to the nanotubes. Note that the SWNT field effect transistor based sensors (or chemFETs) exhibited a higher sensitivity to NO_2 than to NH_3.

One key issue for electrical conduction in CNT-based sensors is the metal-carbon nanotube interface. The role electrical conduction at the metal-CNT interface plays on chemical sensing was qualified by Chen et al., by comparing CNT devices under three different configurations: 1) no passivation, 2) metal electrode passivation, and 3) electrode and CNT passivation (*61*). Under no passivation, the chemFETs showed significant conduction changes due to protein adsorption. To isolate protein adsorption at the metal electrodes from that along the carbon nanotubes, the metal electrodes were coated with a biocompatible polymer known for repelling proteins. Subsequent experiments, performed under the same conditions, showed no conductance change due to protein exposure even though AFM images revealed protein adsorption on the carbon nanotubes. Moreover, with both electrodes and carbon nanotubes passivated, no conduction changes were observed. The results of this experiment suggest that conduction changes are dominated by chemical adsorption effects at the metal-carbon nanotube interface and not on the carbon nanotube surface itself. It is believed that adsorption at the metal-CNT interface acts equivalently to a reduction of the metal work function, thus changing the nature of contacts and conduction of the device.

3.2.6 Chem/Bio Sensors

Carbon nanotubes offer many advantages over conventional gas sensors (*62-69*). Although semiconducting metal oxide based sensors are highly sensitive, they require high operating temperature (200 °C – 600 °C) in order to maintain high sensitivity levels (1 - 10 ppm range) (*62*, *65*, *66*). Polymer-based sensors have been observed to offer short response and recovery times; however, the materials to be sensed must be in the liquid state (*62*, *66*). Conducting composite-based materials suffer from limited sensitivity (*62*). Carbon nanotube based sensors can be operated at room temperature, offer greater conductivities, have faster response times, and are sensitive to a larger range of chemicals than traditional gas detectors.

Carbon nanotubes can be potentially used in a wide variety of chemical, gas, and biological detecting sensors. Typically, most sensor applications fall into the chemresistor realm. Carbon nanotube chemresistors fall into two different categories (*58*). The first type uses carbon nanotubes in a “bulk”-type application. The carbon nanotubes are typically used as a filler material in composite materials – so called nanocomposites. The second category uses the carbon nanotube itself as the individual sensing element for the device. The differences between the two device types are discussed below.

3.2.6.1 Nanocomposites

The mixing of carbon nanotubes with traditional bulk materials has led to the development of nanocomposite materials. They have been shown to improve the mechanical, optical, and electrical properties of the matrix materials. For nanocomposite chemresistors, the matrix material is typically polymer-based, although, other materials, such as tin oxide, have been used to make sensors. For these nanocomposite devices, the carbon nanotubes are primarily used to increase the conductivity of the materials. Both single wall and multiwall CNTs can be used. Generally, the matrix material detects the analyte of interest, and the carbon nanotubes embedded in the matrix act as conduction pathways from the matrix to the metal electrodes. A variety of chemicals and biological compounds have been detected using these nanocomposite devices.

Chemical sensors of various device architectures and matrix materials have been fabricated using nanocomposite materials. One such sensor uses functionalized CNT/PMMA (polymethylmethacrylate) dip-coated films, deposited between two interdigital electrodes, as chemresistors (*69*). The electrical response of the chemresistor was measured as the device was exposed to different solvent vapors inside a gas chamber. Initial resistance values ranged between 14,000 and 45,000 kΩ. Increases in resistance – 100 to 1000 times initial values – were observed when exposed to dichloromethane, choloroform, and acetone vapors. The *f*-CNT/PMMA chemresistors showed fast response times (<1s for dichloromethane, ~1s for acetone), and initial output levels were obtained almost immediately upon removal of the solvent vapor. Additionally, the chemresistor was connected to a wireless communication system, and the device behavior was monitored remotely by a nearby computer.

Low resistance gas sensors have been fabricated from multiwall carbon nanotubes/tin oxide mixtures (*70*). The MWNT/SnO_2 mixture was deposited on a ceramic tube between platinum electrodes and tested for its electrical response to NO, NO_2, ethanol and acetylene. A change in resistance was detected for nitric oxide levels as low as 2 ppm. The resistance for NO_2 was 230 kΩ at 2 ppm and increased to 2.8 MΩ at 50 ppm. Resistance changes were also observed for ethanol and acetylene levels as low as 10 ppm. In fact, the resistance actually decreased as the gas concentrations increased. The resistance of the sensor when exposed to 10 ppm of ethanol was 71 kΩ. It decreased to 23 kΩ when exposed to 1000 ppm of ethanol. The resistance increase or decrease corresponds to whether the gas is oxidizing (NO, NO_2) or reducing (ethanol, acetylene), respectively. The gas detection mechanism for this sensor is the interaction between the tin oxide nanograins and the adsorbed molecules (see the metal oxide section for more details). The MWNTs serve as low resistance, metal-like conductive pathways for electron transport away from the tin oxide nanograins.

3.2.6.2 Carbon Nanotube Sensing Devices

In contrast to the nanocomposites, the next class of chemresistor sensors uses carbon nanotubes as the actual sensing element. The analyte species is adsorbed onto the carbon nanotube either by chemical bonding or physical attraction. Upon adsorption, a change in electrical conduction through the nanotubes is observed due to charge transfer, capacitive changes, or some other mechanism. The geometry of the chemresistor sensor devices is largely dependent upon whether the sensing elements are arrays/bundles of carbon nanotubes or individual single-/multi-wall carbon nanotubes.

Arrays and/or bundles of carbon nanotubes have been used for chemresistor devices (*63*, *67*, *71*, *72*). Typically, metal electrodes, usually platinum (Pt), are lithographically defined on a substrate. The carbon nanotubes are then deposited onto the electrodes via CVD, PECVD, or dip/drop-coating from a CNT-solvent solution. Valentini et al., fabricated nitric oxide chemresistor sensors and were able to detect changes in resistance for gas concentrations as low as 5 ppb NO_2 (*72*). It was observed that the more defective nanotubes achieved greater sensitivities to the gas molecules than non-defective nanotubes. Lu et al., fabricated a chemresistor that used palladium (Pd) nanoparticle loaded SWNT bundles as the sensing element for methane detection (*63*). The Pd-loaded SWNTs were drop-coated onto interdigitated electrodes. The Pd nanoparticles increased the sensitivity of the device by assisting in the charge transfer between the adsorbed methane molecule and the carbon nanotube. Slight changes in current were detected as the sensor was exposed to methane gas in concentrations from 6 to 100 ppm; however, the magnitude of the change did not scale with concentration. Both sensors were unable to recover to baseline values after exposure to the gas analyte.

Carbon nanotubes can also serve as the channel in a chemFET structure. In this case the nanotube is connected to two metal electrodes which act as the source and drain of the transistor. The carbon nanotube FETs are fabricated in two different ways. Typically, carbon nanotubes are grown first, then electrodes are fabricated using standard lithography techniques on top of the CNTs (*61*, *64*, *73*). However, there have been "quasi-successful" attempts to first deposit the electrodes, then grow the carbon nanotubes tubes across the metal electrodes (*74*, *75*).

Once fabricated, the chemFETs could be tested in either air, usually for the detection of gases and chemicals, or in liquid, usually for the detection of biological based compounds. Star et al., developed a chemFET that was functionalized with an ion-exchange Nafion polymer to act as a humidity detector (*73*). It was shown that the modulation (expressed as the ratio between the "on" and "off" source-drain current at –10 V and +10 V gate voltages) of the devices approached zero when the humidity levels reached 27% and higher. Chen et al., used a similar geometry to explore the sensing mechanism of carbon nanotubes to protein adsorption (*61*). The SWNTs were contacted using two electrodes and submerged into a liquid solution. A Pt wire was inserted into the solvent and acted as the gate. With no protective coatings applied to the device, a change in the drain-source current was detected when exposed to a variety of proteins. By varying the gate voltage, the conductance of the device was modulated from ~230 nA to near depletion (zero conductance). No change in current was detected for similar devices when both the contact metal and the metal/carbon nanotube interfaces were coated. SWNT chemFETs fabricated by Kong et al., were found to be extremely sensitive to NO_2 and NH_3 (*64*). Upon exposure to NO_2, the conductance of the devices increased by three orders of magnitude.

3.2.6.3 Electrochemical Sensors

Carbon nanotubes can also detect biomolecules electrochemically, by enhancing their electrochemical reactivity (*76-92*). Nanotubes are especially attractive for this role because of their extremely small size, high surface area, high conductivity, and their exceptional chemical and biochemical stability (*76*, *78*, *82*). They are usually configured as high-density CNT arrays, each nanotube modified with distinct chemical or biomolecular recognition elements, and in close proximity to a physical transducer. The goal, then, is to convert the selective chemical or biological recognition event into a useful electrical signal. Generally speaking, CNTs play a dual role in a biosensor, both as immobilization matrices and as an electron mediator, carrying charge to the transducing electrode (*76*). According to Wang (*76*), they can also promote electron transfer reactions, particularly in proteins, even when the redox center is buried deep within the glycoprotein shell. This feature is quite important, since the electron transfer step in electrochemistry can typically only occur for species within 1 nanometer of an electrode surface. The review paper by Wang (*76)* has an excellent description of the variety of CNT-based electrochemical sensors that have been recently studied. CNT-based enzyme electrodes have been fabricated by casting solubilized CNT solutions onto an electrode surface, by self-assembling or growing (*85*) short aligned SWNTs perpendicular to an electrode surface, and by preparing CNT-based biocomposite electrodes including screen-printed CNT-based inks.

Li et al., (*79*) and Tu et al., (*93*) have shown recent success in developing CNT nanoelectrode arrays for biosensing. While many CNT sensor arrays use randomly oriented mats of CNTs with a large 3-D exposed surface area, Li et al., argue that, for many applications, including ultrasensitive electroanalysis, the electrode area should be minimized, since noise comes from the capacitative charging-discharging current which is proportional to electrode area. They first deposit a metal contact plane, then an ultrathin catalyst film to grow an aligned array of short (~5 microns) nanotubes, then a SiO_2 layer to encapsulate them. A chemical-mechanical polishing (CMP) step then reveals and opens the CNTs. By carefully controlling these steps, a low-density array of MWNTs (~10^7 CNTs/cm^2) is created. The open nanotube ends are finally terminated with a carboxylic group to serve as chemically active sensor sites, and can be functionalized later by amine-terminated biomolecules through amide bonds to the carboxylic groups. Li et al., point out that the ideal array is relatively low density, with an inter-element distance greater than the width of the diffusion layer at each element, yielding a steady-state diffusion-limited current mode. Tu et al., (*93*) reported using a similar approach, but spun on an epoxy resin instead of depositing SiO_2.

3.2.6.4 Other Sensor Devices

Although chemresistors are the most widely fabricated sensors using carbon nanotubes, there are other device types that are currently being explored as CNT gas sensors. One such device type is CNT-based resonators. A shift in the resonance frequency of the device is measured upon exposure to the gas analyte. Carbon nanotubes, either in a mat form or as a nanocomposite, are used as the individual sensing element. Chopra et al., fabricated a CNT resonant circuit sensor for ammonia detection (*66*). Single and/or multiwall carbon nanotubes were coated on top of a circular copper disk using epoxy. A decrease in resonant frequency (3–5 MHz) upon the exposure of ammonia was detected for both the SWNT and MWNT resonators, although the SWNT-based sensors showed greater sensitivity than the MWNT-based one. For both resonator types, the magnitude of the frequency shift increased with increasing ammonia concentrations. It is believed that a dielectric constant change is responsible for the resonant frequency shift. Penza et al., also used the resonator approach for fabrication of alcohol sensors (*65*). Here, Langmuir-Blodgett films or mats of single wall carbon nanotubes were deposited on quartz crystal microbalance sensors. Upon exposure to vapor pressures of ethanol and methanol at 59 mm Hg, frequency shifts in the 100 s of hertz were detected. Unfortunately, saturation effects for the sensors were observed at higher vapor pressures.

Gas ionization sensors are another potential application for carbon nanotubes. They work by generating strong electric fields at a sharp tip (typically metal) that causes the breakdown of gas molecules. Carbon nanotubes are advantageous relative to traditional metals because they can generate high electric fields at low applied voltages. Different approaches have been taken to fabricate CNT-based field ionization gas detectors. One approach involved growing multiwall carbon nanotubes by catalytic decomposition of acetylene onto a stainless steel wire (*94*). At applied voltages of 7.5 or 8 kV, helium detection was observed at count rates two orders of magnitude greater than background. In another approach, Modi et al., fabricated a gas ionization sensor able to detect and distinguish between different gases, such as helium, argon, air, carbon dioxide, nitrogen, oxygen, and even ammonia (*95*). The device is made using two electrodes separated by a glass insulator. An aluminum plate acts as the cathode, and vertically aligned MWNTs grown on top of a silicon substrate act as the anode. Unlike typical chemresistors which rely on the absorption/desorption of the gas species, the breakdown voltage of the device, when exposed to the analyte, acts as a unique fingerprint for the gas to be identified. At breakdown, the magnitude of the device discharge current can be correlated to the relative concentration of the analyte. The breakdown voltage for the device is also dependent upon the separation between the two electrodes.

3.2.7 Sensitivity

Thus far, carbon nanotube based sensors have been used to detect a wide variety of gases, chemicals, biological compounds and proteins. Inert gases, such as helium, argon, and nitrogen, and organic vapors, such as ethanol, methanol, and acetone, have been tested. The presence and concentration modulations of glucose, hormones, and other proteins in buffer solutions have also been observed (*61*, *71*). Many of these chemicals have been successfully detected by multiple CNT-based sensor configurations. Each gas sensor type has advantages and disadvantages that affect its performance. Factors such as response time, sensitivity, and reversibility, ultimately determine the gas level detection limits as well as the effectiveness of the sensors. The detection levels of the sensors varied widely for the analytes tested.

In order to quantify the effectiveness of the CNT-based sensors, the term *sensitivity* is defined as the ratio of the resistance after exposure and before exposure (R_{after}/R_{before}). For conditions where the conductance increases upon exposure, the sensitivity definition is reversed (R_{before}/R_{after}). Sensitivities between 3 and 1000 were achieved for the sensors discussed above. ChemFETs made from individual SWNTs showed very high sensitivities, with values ranging between 10 and 1000, depending upon the analyte (*64*). When exposed to 200 ppm NO_2, chemFET sensitivities of 1000 were obtained (*64*). Unlike typical metal oxide based sensors which require high operating temperatures (250 °C), these devices have the advantage of room temperature operation. Chemresistors have also been shown to exhibit a wide range of sensitivities, which strongly depend upon the concentration and type of the gas analyte (*67, 69, 70, 72*). For example, a SnO_2/MWNT nanocomposite showed sensitivity values between 2 to 20 for NO_2 concentrations between 2 and 50 ppm, respectively (*70*). The same nanocomposite sensor registered a sensitivity value of only 6 when exposed to 1000 ppm of ethanol. Bulk SWNT mats, grown by laser ablation, only showed sensitivity values of approximately 2 when exposed to a 200 ppm flow of NO_2 (*64*). The large difference in sensitivities between the bulk mat and the chemFET values is attributed to the difference between the amounts of carbon nanotube surface area exposed to gas analyte.

As mentioned above, the gas analyte does play a role in determining the sensitivity of the sensors. A difference in response has been observed for polar versus nonpolar molecules as well as oxidizing versus reducing gases (*66*, *69*, *70*). A CNT/PMMA nanocomposite chemresistor showed a strong sensitivity to dichloromethane, choloroform, and acetone with values ranging from 84 to 809; however, no electric response was detected when exposed to toluene and hexane (*69*). For this device, the selectivity was thought to originate with the PMMA and not the carbon nanotubes. The solubility of the chemicals in PMMA was found to be the strongest factor in whether a substantial resistance change was observed. For the resonator-based sensors, a larger shift in the resonance frequency was observed when exposed to polar gases, such as carbon monoxide and ammonia, than when the sensor was exposed to nonpolar gases, such as helium and argon (*68*). Because the frequency shift is related to the dielectric constant, it was found that the magnitude of the shift scales with the dipole moment of the gas. Even the chemFETs showed sensitivity preferences among analytes. ChemFETs that demonstrated sensitivity values of 1000 when exposed to 200 ppm NO_2 only exhibited values between 10 to 100 when exposed to 1% NH_3 in air/argon (*64*). It is believed that two different sensing mechanisms are responsible for the difference.

Another factor that affects sensor detection is the response time. The response time is typically defined as the time duration for the resistance to change by one order of magnitude. The response time for the sensors is strongly dependent upon the concentration of the analyte. For example, SWNT chemFETs exhibited responses times of 600 sec, 60 sec, and 2 to 10 sec when exposed to 2, 20, and 200 ppm NO_2, respectively (*64*). These times are similar to those exhibited by other carbon nanotube based sensors and are comparable to high performance metal oxide detectors, which have response times of ~50 sec.

The biggest issue affecting the sensitivity of the gas detectors is reversibility. Reversibility is defined as the ability of the sensor to recover to baseline (pre-exposure) values after exposure to the gas analyte. A majority of the carbon nanotube based sensors discussed here exhibited irreversibility. For example, the SWNT chemFETs exhibited recovery times of ~12 hours after exposure to NO_2 (*64*). Chopra et al., initially reported that the CNT-epoxy resonators were able to recover in only 10 minutes; however, these resonators were only sensitive to ammonia and not the inert gases (*66*). In fact, the only CNT-based sensors that exhibited strong reversibility were the nanocomposite chemresistors. This is most likely due to the fact that the carbon nanotubes in the nanocomposites are primarily used for electric conduction and not for chemical sensing.

One assumption plaguing the irreversibility of the devices is that the pre-exposure state of the carbon nanotubes is pristine (i.e., free of any adsorbed species). Valentini et al., fabricated and tested vertically aligned MWNT-based chemresistors at NO_2 concentrations between 5 ppb to 500 ppb at 165 °C (*72*). Although resistance changes due to nitric oxide exposure were observed, the baseline (no gas exposure) resistance level of the device steadily increased or decreased throughout the entire experiment. In the CNT-epoxy resonators discussed previously, no resonant frequency shift was observed when exposed to inert gases, such as helium, argon, or nitrogen; however, upon high temperature vacuum annealing, these devices exhibited frequency shifting when exposed to the inert gases (*66*, *68*). For both of these devices, residual adsorbates present on the sensors prevented the sensors from achieving their full sensitivity.

The solution to the irreversibility problem is to remove any adsorbed analyte from the carbon nanotube. Carbon nanotubes are ideal candidates for sensors because they adsorb, physically or chemically, a wide array of gases, chemicals, elements, biological compounds, and proteins. In fact, the carbon nanotubes readily adsorb oxygen. Removal of any residual adsorbates on the carbon nanotubes must be performed before and after exposure to guarantee the maximum sensitivity possible. Carbon nanotube adsorbates are typically removed either by annealing, vacuum treating, or ultraviolet (UV) light exposure. ChemFETs recovered in ~1 hour after heating in air at 200 °C (as compared to the ~12 hour recovery time at room temperature) (*64*). Pd loaded chemresistors, tested for methane, were exposed to UV light for 30 minutes (*63*). The energy of the UV light was able to speed up the desorption of the gas molecules on the CNT surface. The UV light drastically increased the resistance of the sensor, exceeding even pre-exposure resistance values.

CNT-based electrochemical sensors have been shown to be remarkably sensitive to species such as glucose, fructose, lactate, polyphenols, ethanol, organophosphate pesticides, trace toxic metals, urea, cholesterol, penicillin, hormones, neurotransmitters, and DNA (*76-79*, *81*, *83*, *84*, *86*, *89*, *91*). Generally speaking, the electrochemically detected products are often NADH or hydrogen peroxide, whose detection limits are currently on the order of 100 nM (*76*). As a biosensor, CNT-based setups have detected DNA sequences consisting of fewer than 1000 strands (*79*). As a chemical sensor, detection limit down to a few nM has been demonstrated for benchmark species $K_4Fe(CN)_6$, which is 100-1000 times better response than conventional electrodes (*79*). One reason for the excellent sensitivity, as well as response time of CNT-based electrochemical sensors, is the small nanotube radius, which leads to a high signal-to-noise ratio and a lower RC time constant (*79*). In the detection of liberated NADH, CNT-based biosensors are resistant to surface fouling associated with NADH oxidation, unlike other techniques, and so have high stability (*76*). The nanoelectrode array developed by Li (*79*), however, suffers from a type of reversibility problem. Biomolecules have a strong nonspecific adsorption on SiO_2 surfaces, and SiO_2 fills 99% of the space surrounding the nanotube electrodes in their arrays. As a result, a rigorous time-consuming washing must be done between measurements. Their solution has been to apply an organic passivation layer to the SiO_2 areas, so that the nanotubes themselves present the only active sites.

3.2.8 Selectivity

As mentioned previously, carbon nanotubes can be used for sensing a wide range of gases, chemicals, and biological compounds. While this makes carbon nanotubes attractive for a number of applications, this diversity can be a hindrance when a specific chemical detector is desired. The selectivity of the carbon nanotubes must be improved in order to make these devices into reliable and chemical specific detectors. There are two approaches to solving the selectivity issues with carbon nanotubes. The first approach involves creating devices that avoid this issue. For example, the gas ionization sensor proposed by Modi et al., operates on the principle of gas electric field breakdown and does not require any special treatment of the nanotubes (*95*). The second approach involves functionalization of the carbon nanotubes.

Functionalization involves the chemical modification of the carbon nanotube surface by chemically attaching a molecule that bonds with specific chemicals. Covalent attachment to the carbon nanotube involves changing the bonding structure from sp^2 to sp^3 and has proven to be difficult due to the inertness of the CNT (*56*). The resulting loss of CNT double-bond conjugation is electronically undesirable, resulting in detrimental effects on carrier transport (*56*). Functionalization of the tubes via noncovalent forces, such as Van der Waals forces, has proven to be the most successful method in functionalizing CNTs and gaining species selectivity as well as increased sensitivity (*56*). Direct functionalization of the sidewalls has been performed using different chemistries, including fluorination, chlorination, and oxidation and by the attachment of various chemical groups, such as atomic hydrogen, aromatic groups, and esters (*56, 96*). Specific functional groups are designed to attach specific compounds and repel others.

Functionalization of carbon nanotubes has been performed for two main reasons. The first reason is to facilitate the carbon-polymer bond in nanocomposite materials and to promote conduction between the polymeric materials and the carbon nanotubes. In one study, this effect was explored using three similar sensing materials - 1) the polymer polythiophene (poly[3-(2-

hydroxyethyl)-2,5-thienylene] or PHET, 2) a CNT/PHET composite, and 3) a composite of the polymer PHET and MWNTs functionalized with PHET (*97*). The room temperature electrical conductivity of the PHET, CNT/PHET, and CNT- *f*-PHET were 10^{-8}, 1.38, and 38 S cm respectively. It is believed that the conductivity differences between the samples are due either to an increased charge transfer interaction between the CNT and PHET, especially with functionalization, or to an increased homogeneity between the *f*-CNT and polymer matrix than in the CNT/PHET composites. The functionalization of carbon nanotubes with polymers has also been used to obtain n-type FETs that are stable in air (*56*).

The second reason for functionalization is to immobilize and detect the presence of biological compounds and proteins. It has been shown that many types of proteins adsorb onto carbon nanotubes via nonspecific binding (*61*, *71*, *98*). Functionalization can be used to detect a wide range of biological compounds, proteins, or a specific biochemical. Lin et al., were able to functionalize carbon nanotube tips with glucose detecting enzymes via “carbodiimide chemistry by forming amide linkages between amine residues and carboxylic acid groups” (*71*). The electrochemical-based biosensor was able to detect the presence of glucose even in the presence of interferents, such as acetaminophen and ascorbic acids. Biospecific pairs are also used for selective biomolecular detection. For example, Chen et al., were able to make CNT sensors for the detection of hormones via the antigen/antibody binding pair (*61*). In particular, carbon nanotubes were functionalized by adsorption of a hCG antigen. hCG - human chorionic gonadotropin - is a hormone produced in women during pregnancy and is used in clinical tests for detection and determination of pregnancy. Once adsorbed with the hCG antigen, no conduction change was exhibited upon exposure to other structurally similar hormones, such as rabbit pregnancy hormones. However, a signal change proportional to concentration was observed when exposed to the α-hCG antibody, indicating successful binding.

3.2.9 Conclusions

A number of papers have been published on sensors using carbon nanotubes. In general, it is the matrix material or overlayer on the nanotubes which actually detects the analyte of interest, and this induces a change in conduction in the nanotubes themselves. In at least some cases, more defective nanotubes have been demonstrated to achieve greater sensitivities to analytes than non-defective nanotubes. Carbon nanotube adsorbates are typically removed either by annealing, vacuum treating, or UV light exposure.

Of the problems observed, the lack of reversibility may be the most significant and pervasive. In fact, the only CNT-based sensors that exhibited strong reversibility were the nanocomposite chemresistors. This seems to be due to the CNT’s limited role in those devices of electric conduction and not chemical sensing. There were also reports of nonlinearity, where the magnitude of a change did not scale with the concentration of the analyte. In a report on a CNT-based humidity detector, it was shown that the on/off modulation approached zero when the humidity levels reached 27% and higher. Such restricted performance is insufficient for typical sensor requirements.

4. Summary

Since chemical adsorption depends on surface area, and power consumption is directly related to the size of the device, small devices with large surface areas are desirable for use in autonomous chemical sensors that can provide both the Army as well as civilian homeland security entities with a distinct strategic advantage. Nanoscale materials and devices hold promise because they possess surface area to volume ratios that are impossible to achieve in bulk materials. Research in the area of nanoelectronic devices for chemical sensing is in its relative infancy, and is an active area which has increased dramatically in the past decade. Although in general, nanoscale sensors have as yet demonstrated limited selectivity to a specific analyte, organic and inorganic nanowire devices have shown sensitivity to large groups, or classes, of chemicals. This is promising evidence, and suggests pathways for continued research to achieve the goal of viable sensor platforms. While efforts to engineer the devices and the sensing materials to be more selective will continue, the selectivity of some or all of the approaches described in this report could be further enhanced by using an array of different sensors with more intricate interrogation algorithms to determine the analyte responsible for a signal with greater precision.

Response times in the tens of seconds and recovery times as low as one minute have been reported for nanowire sensors, comparing favorably to those reported for bulk and thin film sensors. With anticipated advances in nanoscale circuit design and technology, the time constants for nanowire sensing devices have the potential to improve dramatically over current bulk and thin film sensors. UV light, elevated temperatures and strong gate pulses may be integrated into device designs to improve refresh rates for the nanowire sensor platforms. However, the effects of these reset mechanisms in terms of irreversible damage to the nanoscale active sensing element will need to be investigated and understood in the context of their reduced scale. Single wire and multiple wire devices have been demonstrated, and are anticipated to have distinct application areas. Single wire devices promise the fastest speeds and lowest power consumption while holding the potential for single molecule detection, making them candidates for high precision sensing applications. Multiple wire devices may be more reliable and robust in addition to being easier to fabricate, and may be most useful in pre-screening or disposable sensing applications.

While the field of nanoelectronic sensing is currently in the realm of basic research, it is prudent to look forward to a number of technological issues that must be addressed for nanoelectronic sensing technology to become viable. These include stability of the nanowire active element and the sensing circuit as a whole, contact effects, packaging design, power requirements, and reproducibility. Fabrication requirements dictate the need to align, self-assemble or selectively grow nanowires for economical integration into device and circuit architectures. Contact and interface technology must be understood at the atomic level to ensure reliable transport in the nanowire sensor element and maximize signal to noise ratio in the device. Analyte sensing mechanisms for a particular nanowire approach must be well understood, since multiple reaction pathways available to an analyte will complicate the calculation of surface concentration from the measured conductance, thus reducing both sensitivity and selectivity. Circuit designs must be developed to capitalize on the potential of nanowire sensing elements, and to overcome any of their potential limitations, e.g., by building in redundancy and fault tolerance. Fluidic delivery mechanisms and thermal management will be critical elements of packaging design, especially for discrete nanowire devices.

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5. References

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1. Senecal, A. private communication.

2. Joint Science and Technology Office Chemical and Biological Defense, Call for proposals to the Physical Science and Technology (S&T) Chemical and Biological Defense Program (CBDP) for FY2007.

3. Li, Z.; Rajendran, B.; Kamins, T. I.; Li, X.; Chen, Y.; Williams, R. S. Silicon nanowires for sequence-specific DNA sensing: device fabrication and simulation. *Applied Physics A – Materials Science & Processing* **2005**, *80* (6), 1257–1263.

4. Gerard, M.; Chaubey, A.; Malhotra, B. D. Application of conducting polymers to biosensors. *Biosensors and Bioelectronics* **2002**, *17* (5), 345–359.

5. Mulla, I. S.; Ramgir, N. S.; Hwang, Y. K.; Chang J. S. Semiconductor tin oxide gas sensors: From bulk to thin films. *Journal of Industrial and Engineering Chemistry* **2004**, *10* (7), 1242–1256.

6. Wang, Z. L. Zinc oxide nanostructures: growth, properties and applications. *Journal of Physics - Condensed Matter* **2004**, *16* (25), R829–R858.

7. Wang, Z. L. Functional oxide nanobelts: Materials, properties and potential applications in nanosystems and biotechnology. *Annual Review of Physical Chemistry* **2004**, *55,* 159–196.

8. Wang, Z. L.; Kong, X. Y.; Ding, Y.; Gao, P. X.; Hughes, W. L.; Yang, R. S.; Zhang, Y. Semiconducting and piezoelectric oxide nanostructures induced by polar surfaces. *Advanced Functional Materials* **2004**, *14* (10), 943–956.

9. Wang, X. D.; Summers, C. J.; Wang, Z. L. Mesoporous single-crystal ZnO nanowires epitaxially sheathed with Zn_2SiO_4. *Advanced Materials* **2004**, *16* (14), 1215.

10. Liu, Y.; Liu, M. Growth of aligned square-shaped SnO_2 tube arrays. *Advanced Functional Materials* **2005**, *15* (1), 57–62.

11. Islam, M. S.; Sharma, S.; Kamins, T. I.; Williams, R. S. A novel interconnection technique for manufacturing nanowire devices. *Applied Physics A - Materials Science & Processing* **2005**, *80* (6), 1133–1140.

12. Bauer, L. A.; Birenbaum, N. S.; Meyer, G. J. Biological applications of high aspect ratio nanoparticles. *Journal of Materials Chemistry* **2004**, *14* (4), 517–526.

13. Rajeshwar, K.; de Tacconi, N. R.; Chenthamarakshan, C. R. Spatially directed electrosynthesis of semiconductors for photoelectrochemical applications. *Current Opinion in Solid State & Materials Science* **2004**, *8* (3–4), 173–182.

14. Han, X. H.; Wang, G. Z.; Jie, J. S.; Choy, W. C. H.; Luo, Y.; Yuk, T. I.; Hou, J. G. Controllable synthesis and optical properties of novel ZnO cone arrays via vapor transport at low temperature. *Journal of Physical Chemistry B* **2005**, *109* (7), 2733–2738.

15. Fan, Z. Y.; Wang, D. W.; Chang, P. C.; Tseng, W. Y.; Lu, J. G. ZnO nanowire field-effect transistor and oxygen sensing property. *Applied Physics Letters* **2005**, *85* (24), 5923–5925.

16. Yoo, S.; Akbar, S. A.; Sandhage, K. H. Nanocarving of titania (TiO_2): a novel approach for fabricating chemical sensing platform. *Ceramics International* **2004**, *30* (7 Sp. Iss. SI), 1121–1126.

17. Kolmakov, A.; Moskovits, M. Chemical sensing and catalysis by one-dimensional metal-oxide nanostructures. *Annual Review of Materials Research* **2004**, *34*, 151–180.

18. Sau, T. K.; Murphy, C. J. Seeded high yield synthesis of short Au nanorods in aqueous solution. *Langmuir* **2004**, *20* (15), 6414–6420.

19. Gao, T.; Li, Q. H.; Wang, T. H. Sonochemical synthesis, optical properties, and electrical properties of core/shell-type ZnO nanorod/CdS nanoparticle composites. *Chemistry of Materials* **2005**, *17* (4), 887–892.

20. Ma, Y. J.; Zhou, F.; Lu, L.; Zhang, Z. Low-temperature transport properties of individual SnO_2 nanowires. *Solid State Communications* **2004**, *130* (5), 313–316.

21. Schlecht, U.; Guse, B.; Raible, I.; Vossmeyer, T.; Burghard, M. A direct synthetic approach to vanadium pentoxide nanofibres modified with silver nanoparticles. *Chemical Communications* **2004**, *2004* (19), 2184–2185.

22. Zhang, Y.; Kolmakov, A.; Lilach, Y.; Moskovits, M. Electronic control of chemistry and catalysis at the surface of an individual tin oxide nanowire. *Journal of Physical Chemistry B* **2005**, *109* (5), 1923–1929.

23. Fan, Z. Y.; Lu, J. G. Gate-refreshable nanowire chemical sensors. *Applied Physics Letters* **2005**, *86* (12), 123510.

24. Gao, T.; Li, Q. H.; Wang, T. H. Sonochemical synthesis, optical properties, and electrical properties of core/shell-type ZnO nanorod/CdS nanoparticle composites. *Chemistry of Materials* **2005**, *17* (4), 887–892.

25. Wan, Q.; Li, Q. H.; Chen, Y. J.; Wang, T. H.; He, X. L.; Li, J. P.; Lin, C. L. Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors. *Applied Physics Letters* **2004**, *84* (18), 3654–3656.

26. Chu, X. F.; Jiang, D. L.; Djurisic, A. B.; Yu, H. L. Gas-sensing properties of thick film based on ZnO nano-tetrapods. *Chemical Physics Letters* **2005**, *401* (4–6), 426–429.

27. Yu, M. F.; Atashbar, M. Z.; Chen, X. L. Mechanical and electrical characterization of beta-Ga_2O_3 nanostructures for sensing applications. *IEEE Sensors Journal* **2005**, *5* (1), 20–25.

28. Tang, T.; Liu, X. L.; Li, C.; Lei, B., Zhang, D. H.; Rouhanizadeh, M.; Hsiai, T.; Zhou, C. W. Complementary response of In_2O_3 nanowires and carbon nanotubes to low-density lipoprotein chemical gating. *Applied Physics Letters* **2005**, *86* (10), 103903.

29. Katz, H. E. Chemically sensitive field-effect transistors and chemiresistors: New materials and device structures. *Electroanalysis* **2004**, *16* (22), 1837–1842.

30. Zhang, D. H.; Liu, Z. Q.; Li, C.; Tang, T.; Liu, X. L.; Han, S.; Lei, B.; Zhou, C. W. Detection of NO_2 down to ppb levels using individual and multiple In_2O_3 nanowire devices. *Nano Letters* **2004**, *4* (10), 1919–1924.

31. Arnold, M. S.; Avouris, P.; Pan, Z. W.; Wang, Z. L. Field-effect transistors based on single semiconducting oxide nanobelts. *Journal of Physical Chemistry B* **2003**, *107* (3), 659–663.

32. Lin, Y. H.; Cui, X. L.; Li, L. Y. Low-potential amperometric determination of hydrogen peroxide with a carbon paste electrode modified with nanostructured cryptomelane-type manganese oxides. *Electrochemistry Communications* **2005**, *7* (2), 166–172.

33. Kang, B. S.; Ren, F.; Heo, Y. W.; Tien, L. C.; Norton, D. P.; Pearton, S. J. pH measurements with single ZnO nanorods integrated with a microchannel. *Applied Physics Letters* **2005**, *86* (11), 112105.

34. Zhou, J.; Fisher, E. R. Synthesis and properties of plasma-polymerized polypyrrole/Au composite nanofibers. *Journal of Nanoscience and Nanotechnology* **2004**, *4* (5), 539–547.

35. Hahm, J.; Lieber, C. Direct ultrasensitive electrical detection of DNA and DNA sequence variations using nanowire nanosensors. *Nano Letters* **2004**, *4* , 51–54.

36. Patolsky, F.; Zheng, G.; Hayden, O.; Lakadamyali, M.; Zhuang, X.; Lieber, C. Electrical detection of single viruses. *Proceedings of the National Academy of Sciences* **2004**, *101,* 14017–14022.

37. Wang, W.; Chen, C.; Lin, K.; Fang, Y.; Lieber, C. Label-free detection of small-molecule-protein interactions by using nanowire nanosensors. *Proceedings of the National Academy of Sciences* **2005**, *102,* 3208–3212.

38. Wu, Y.; Cui, Y.; Huynh, L.; Barrelet, C. J.; Bell, D. C.; Lieber, C. M. Controlled growth and structures of molecular-scale silicon nanowires. *Nano Letters* **2004**, *4* (3), 433–436.

39. Meng, G. W.; Cao, A. Y.; Cheng, J. Y.; Ajayan, P. M. Carbon nanotubes grafted on silicon oxide nanowires. *Journal of Nanoscience and Nanotechnology* **2004,** *4* (7), 712–715.

40. Seong, H. K.; Choi, H. J.; Lee, S. K.; Lee, J. I.; Choi, D. J. Optical and electrical transport properties in silicon carbide nanowires. *Applied Physics Letters* **2004**, *85* (7), 1256–1258.

41. Beckman, R. A.; Johnston-Halperin, E.; Melosh, N. A.; Luo, Y.; Green, J. E.; Heath, J. R. Fabrication of conducting Si nanowire arrays. *Journal of Applied Physics* **2004**, *96* (10), 5921–5923.

42. Li, Z.; Chen, Y.; Li, X.; Kamins, T. I.; Nauka, K., Williams, R. S. Sequence-specific label-free DNA sensors based on silicon nanowires. *Nano Letters* **2004**, *4* (2), 245–247.

43. Zhou, Y.; Freitag, M.; Hone, J.; Staii, C.; Johnson, Jr., A. T.; Pinto, N. J.; MacDiarmid, A. G. Fabrication and electrical characterization of polyaniline-based nanofibers with diameter below 30 nm. *Applied Physics Letters* **2003**, *83* (18), 3800–3802.

44. Covington, J. A.; Gardner, J. W.; Bartlett, P. N.; Toh, C-S. Conductive polymer gate FET devices for vapour sensing. *IEE Proceedings - Circuits Devices and Systems* **2004**, *151* (4), 326–334.

45. Crone, B.; Dodabalapur, A.; Gelperin, A.; Torsi, L.; Katz, H. E.; Lovinger, A. J.; Bao, Z. Electronic sensing of vapors with organic transistors. *Applied Physics Letters* **2001**, *78* (15), 2229–2231.

46. Torsi, L.; Lovinger, A. J.; Crone, B.; Someya, T.; Dodabalapur, A.; Katz, H. E.; Gelperin, A. Correlation between oligothiophene thin film transistor morphology and vapor responses. *Journal of Physical Chemistry* **2002**, *106* (48), 12563–12568.

47. Covington, J. A.; Gardner, J. W.; Briand, D.; de Rooij, N. F. A polymer gate FET sensor array for detecting organic vapours. *Sensors and Actuators B* **2001**, *77* (1–2), 155–162.

48. Malliaras G.; Friend, R. An organic electronics primer. *Physics Today* **2005**, *58* (5), 53–57.

49. Torsi, L.; Lovinger, A. J.; Crone, B.; Someya, T.; Dodabalapur, A.; Katz, H. E.; Gelperin, A. Correlation between oligothiophene thin film transistor morphology and vapor responses. *Journal of Physical Chemistry B* **2002**, *106* (48), 12563–12568.

50. Scott, J. C. Metal–organic interface and charge injection in organic electronic devices. *Journal of Vacuum Science and Technology A* **2003**, *21* (3), 521–31.

51. Hosseini, A. R.; Wong, M. H.; Shen, Y.; Malliaras, G. G. Charge injection in doped organic semiconductors. *Journal of Applied Physics* **2005**, *97* (2), 023705.

52. Joseph, Y.; Guse, B.; Yasuda, A.; Vossmeyer, T. Chemiresistor coatings from Pt- and Au-nanoparticle/nonanedithiol films: sensitivity to gases and solvent vapors. *Sensors and Actuators B* **2004**, *98* (2–3), 188–195.

53. This is based on toxicity data from the World Health Organization. http://www.who.int/csr/delibepidemics/annex1.pdf.

54. Chen, S. G.; Hu, J. W.; Zhang, M. Q.; Rong, M. Z. Effects of temperature and vapor pressure on the gas sensing behavior of carbon black filled polyurethane composites. *Sensors and Actuators B* **2005**, *105* (2), 187–193.

55. Dai, H. J. Carbon nanotubes: opportunities and challenges. *Surface Science* **2002**, *500* (1-3), 218–241.

56. Dai, H. J. Carbon nanotubes: synthesis, integration, and properties. *Accounts of Chemical Research* **2002**, *35* (12), 1035–1044.

57. Wang, Y.; Kim, M. J.; Shan, H.; Kittrell, C.; Fan, H.; Ericson, L. M.; Hwang, W.-F.; Arepalli, S.; Hauge, R .H.; Smalley, R. E. Continued growth of single-walled carbon nanotubes. *Nano Letters* **2005**, *5* (6), 997–1002.

58. Melechko, A. V.; Merkulov, V. I.; McKnight, T. E.; Guillorn, M. A.; Klein, K. L.; Lowndes, D. H.; Simpson, M. L. Vertically aligned carbon nanofibers and related structures: Controlled synthesis and directed assembly. *Journal of Applied Physics*, **2005**, *97* (4), 041301.

59. Ajayan, P. M. Nanotechnology: How does a nanofibre grow? *Nature* **2004**, *427* (5), 402.

60 Durkop, T.; Getty, S. A.; Cobas E.; Fuhrer, M. S. Extraordinary mobility in semiconducting carbon nanotubes. *Nano Letters* **2004**, *4* (1), 35–39.

61. Chen, R. J.; Choi, H. C.; Bangsaruntip, S.; Yenilmez, E.; Tang, X.; Wang, Q.; Chang, Y.-L.; Dai, H. An investigation of the mechanisms of electronic sensing of protein adsorption on carbon nanotube devices. *Journal of the American Chemical Society* **2004**, *126* (5), 1563–1568.

62. Grujicic, M.; Cao, G.; Roy, W. N. A computational analysis of the carbon-nanotube-based resonant-circuit sensors. *Applied Surface Science* **2004**, *229* (1–4), 316.

63. Li, Y. J.; Han, J.; Ng, H.-T.; Binder, C.; Partridge, C.; Meyyappan, M. Room temperature methane detection using palladium loaded single-walled carbon nanotube sensors. *Chemical Physics Letters* **2004**, *391* (4-6), 344–348.

64. Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. Nanotube molecular wires as chemical sensors. *Science* **2000**, *287* (4), 622–625.

65. Penza, M.; Cassano, G.; Aversa, P.; Antolini, F.; Cusano, A.; Cutolo, A.; Giordano, M.; Nicolais, L. Alcohol detection using carbon nanotubes acoustic and optical sensors. *Applied Physics Letters* **2004**, *85* (12), 2379–2381.

66. Chopra, S.; Pham, A.; Gaillard, J.; Parker, A.; Rao, A. M. Carbon-nanotube-based resonant-circuit sensor for ammonia. *Applied Physics Letters* **2002**, *80* (24), 4632–4634.

67. Valentini, L.; Bavastrello, V.; Stura, E.; Armentano, I.; Nicolini C.; Kenny, J. M. Sensors for inorganic vapor detection based on carbon nanotubes and poly(o-anisidine) nanocomposite material. *Chemical Physics Letters* **2004**, *383* (5–6), 617–622.

68. Chopra, S.; McGuire, K.; Gothard, N.; Rao, A. M.; Pham, A. Selective gas detection using a carbon nanotube sensor. *Applied Physics Letters* **2003**, *83* (11), 2280–2282.

69. Abraham, J. K.; Philip, B.; Witchurch, A.; Varadan, V. K.; Reddy, C. C. A compact wireless gas sensor using a carbon nanotube/PMMA thin film chemiresistor. *Smart Materials and Structures* **2004**, *13* (4), 1045–1049.

70. Liang, Y. X.; Chen Y. J.; Wang, T. H. Low-resistance gas sensors fabricated from multiwalled carbon nanotubes coated with a thin tin oxide layer. *Applied Physics Letters* **2004**, *85* (4), 666–668.

71. Lin, Y. H.; Lu, F.; Tu, Y.; Ren, Z. F. Glucose biosensors based on carbon nanotube nanoelectrode ensembles. *Nano Letters* **2004**, *4* (2), 191–195.

72. Valentini, L.; Mercuri, F.; Armentano, I.; Cantalini, C.; Picozzi, S.; Lozzi, L.; Santucci, S.; Sgamellotti, A.; Kenny, J. M. Role of defects on the gas sensing properties of carbon nanotubes thin films: experiment and theory. *Chemical Physics Letters* **2004**, *387* (4–6), 356-361.

73. Star, A.; Han, T. R.; Joshi, V.; Stetter, J. R. Sensing with Nafion Coated Carbon Nanotube Field-Effect Transistors. *Electroanalysis* **2004**, *16* (1-2) 108–112.

74. Tseng, Y.-C.; Xuan, P.; Javey, A.; Malloy, R.; Wang, Q.; Bokor, J.; Dai, H. Monolithic integration of carbon nanotube devices with silicon MOS technology. *Nano Letters* **2004**, *4* (1) 123–127.

75. Franklin, N. R.; Wang, Q.; Tombler, T. W.; Javey, A.; Shim, M.; Dai, H. Integration of suspended carbon nanotube arrays into electronic devices and electromechanical systems. *Applied Physics Letters* **2002**, *81* (5), 913–915.

76. Wang, J. Carbon-Nanotube Based Electrochemical Biosensors: A Review. *Electroanalysis* **2005**, *17* (1), 7–14.

77. Joshi, K. A.; Tang, J.; Haddon, R.; Wang, J.; Chen, W.; Mulchandani, A. A disposable biosensor for organophosphorus nerve agents based on carbon nanotubes modified thick film strip electrode. *Electroanalysis* **2005**, *17* (1), 54–58.

78. Zhao, Q.; Gan, Z.; Zhuang, Q. Electrochemical Sensors Based on Carbon Nanotubes. *Electroanalysis* **2002**, *14* (23), 1609–1613.

79. Li, J.; Koehne, J. E.; Cassell, A. M.; Chen, H.; Ng, H. T.; Ye, Q.; Fan, W.; Han, J.; Meyyappan, M. Inlaid multi-walled carbon nanotube nanoelectrode arrays for electroanalysis. *Electroanalysis* **2005**, *17*(1), 15–27.

80. Atashbar, M. Z.; Bejcek, B.; Singamaneni, S. SWNT network for biomolecule detection. *Materials. Research. Society. Symposium. Proceedings* **2005**, **858E**, HH14.8.1.

81. Cheng, G.; Zhao, J.; Tu, Y.; He, P.; Fang, Y. A sensitive DNA electrochemical biosensor based on magnetite with a glassy carbon electrode modified by multi-walled carbon nanotubes in polypyrrole. *Analytica Chimica Acta* **2005**, *533* (1), 11–16.

82. Lee, C.-S.; Baker, S. E.; Marcus, M. S.; Yang, W.; Eriksson, M. A.; Hamers, R. J. Electrically addressable biomolecular functionalization of carbon nanotube and carbon nanofiber electrodes. *Nano Letters* **2004**, *4* (9), 1713–1716.

83. Li, G.; Liao, J. M.; Hu, G. Q.; Ma, N. Z.; Wu, P. J. study of carbon nanotube modified biosensor for monitoring total cholesterol in blood. *Biosensors and Bioelectronics* **2005**, *20* (10), 2140–2144.

84. Lim, S. H.; Wei, J.; Lin, J. Electrochemical genosensing properties of gold nanoparticle-carbon nanotube hybrid. *Chemical Physics Letters* **2004**, *400* (4–6), 578–582.

85. Sotiropoulou, S.; Chaniotakis, N. A. Carbon nanotube array-based biosensor. *Analytical and Bioanalytical Chemistry* **2003**, *375* (1), 103–105.

86. Tan, X.; Li, M.; Cai, P.; Luo, L.; Zou, X. An amperometric cholesterol biosensor based on multiwalled carbon nanotubes and organically modified sol-gel/chitosan hybrid composite film. *Analytical Biochemistry* **2005**, *337* (1), 111–120.

87. Trojanowicz, M.; Mulchanandi, A.; Mascini, M. Carbon nanotubes-modified screen-printed electrodes for chemical sensors and biosensors. *Analytical Letters* **2004**, *37* (15), 3185–3204.

88. Valentini, F.; Orlanducci, S.; Tamburri, E.; Terranova, M. L.; Curulli, A.; Palleschi G. Single-walled carbon nanotubes on tungsten wires: A new class of microelectrochemical sensors. *Electroanalysis* **2005**, *17* (1), 28–37.

89. Deo, R. P.; Wang, J.; Block, I.; Mulchandani, A.; Joshi, K. A; Trojanowicz, M.; Scholz, F.; Chen, W.; Lin, Y. Determination of organophosphate pesticides at a carbon nanotube/organophosphorus hydrolase electrochemical biosensor. *Analytica Chimica Acta* **2005**, *530* (2), 185–189.

90. Wang, J. Nanomaterial-based electrochemical biosensors. *Analyst* **2005**, *130* (4), 421–426.

91. Ye, J.-S.; Wen, Y.; Zhang, W. D.; Cui, H. F.; Xu, G. Q.; Sheu, F.-S. Electrochemical biosensing platforms using phthalocyanine-functionalized carbon nanotube electrode. *Electroanalysis* **2005**, *17* (1), 89–96.

92. Zhao, Q.; Guan, L.; Gu, Z.; Zhuang, Q. Determination of phenolic compounds based on the tyrosinase-single walled carbon nanotubes sensor. *Electroanalysis* **2005**, *17* (1), 85–88.

93. Tu, Y.; Lin, Y.; Yantasee, W.; Ren, Z. Carbon nanotubes based nanoelectrode arrays: Fabrication, evaluation, and application in voltammetric analysis. *Electroanalysis* **2005**, *17* (1), 79–84.

94. Riley, D. J.; Mann, M.; MacLaren, D. A.; Dastoor, P. C.; Allison, W.; Teo, K.B.K.; Amaratunga, G.A.J.; Milne, W. Helium detection via field ionization from carbon nanotubes. *Nano Letters* **2003**, *3* (10), 1455–1458.

95. Modi, A.; Koratkar, N.; Lass, E.; Wei, B. Q.; Ajayan, P. M. Miniaturized gas ionization sensors using carbon nanotubes. *Nature* **2003**, *424* (2), 171–174.

96, Zhao, J. J.; Xie, R. H. Electronic and Photonic Properties of Doped Carbon Nanotubes. *Journal of Nanoscience and Nanotechnology* **2003**, *3* (6), 459–478.

97. Philip, B.; Xie, J. N.; Chandrasekhar, A.; Abraham, J.; Varadan, V. K. A novel nanocomposite from multiwalled carbon nanotubes functionalized with a conducting polymer. *Smart Materials and Structures* **2004,** *13* (2), 295–298.

98. Wang, J.; Musameh, M. Carbon nanotube screen-printed electrochemical sensors. *Analyst* **2004**, *129* (1), 1–2.

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