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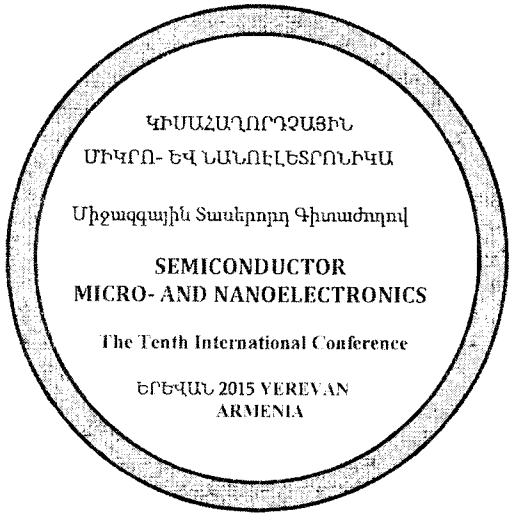

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DECORATED CARBON NANOTUBE SENSORS

V.M. Aroutiounian

Department of Physics of Semiconductors and Microelectronics, Scientific Centre for Semiconductor Devices and Nanotechnologies at Yerevan State University, Yerevan, Armenia
E-mail: ksahar@ysu.am

Carbon nanotubes (CNTs) have been studied extensively and have opened a new science and technology field on nanoscale materials. CNTs are one-dimensional materials: they show many interesting effects and properties. CNTs are graphene sheets of covalently bonded carbon molecules rolled into hollow cylinders. There are two main types of CNTs: single-walled nanotubes (SWCNTs) which have a single carbon layer with a diameter of 1–5 nm and multi-walled nanotubes (MWCNTs) which have multiple layers of carbon (with an interlayer spacing of 0.34 nm), that are concentrically nested together. Multi-walled nanotubes have outer diameters as small as 5.5 nm and inner diameters as small as 2.3 nm. Essentially, CNTs are one-dimensional materials-quantum wires. They have been studied extensively and shown various kinds of size effects in their structures and properties. CNTs demonstrated unique mix of electrical, optical, thermal and mechanical properties. The potential of applications of CNTs is shown in nanoelectronics, sensors, displays, hydrogen storage, batteries etc. A strong demand of cheap, high-sensitive and selective gas sensors involves domestic safety, homeland security, quality control, environmental monitoring et al. The development of CNT based gas sensors and sensor arrays has attracted intensive research interest in the last years because of their potential for the selective and rapid detection of various gaseous species by novel nanostructures integrated in miniature and low-power consuming electronics. More often, the easy CNT configurations as chemiresistors and chemical field effect transistors are used as nanosensors. In these sensors, the electrical properties of nanostructures are dramatically changed when exposed to the target gas analytes. When electron-withdrawing molecules (e.g. NO_2, O_2) or electron-donating molecules (e.g. NH_3) interact with the p-type semiconducting CNTs, they will change the density of holes in the nanotube, which changes the conductance of CNTs. This creates the basis for applications of CNTs as electrical chemical gas sensors. The range of molecules detected by SWCNTs is very limited due to large binding energies and charge transfers with the nanotubes. Some gases (CO, O_2, N_2 and CO_2) and water, for example, do not physicosorb, do not influence on the intrinsic electron spectra and cannot be detected by SWCNTs. For the case of NO_2 and NH_3, they can be physicosorb on the SWCNT surface even at room temperature. Even under high vacuum, the desorption of many gases is too slow for sensor applications; it is necessary to dramatically increase the pre-heating temperature of the work body of the sensor (up to 700K). So, regretfully, gas sensor made of pristine SWCNT has such limitations as low adsorption energy, affinity or long recovery time.

These shortcomings can be, at least in part, circumvented by a CNTs decoration. There are the following approaches for the surface functionalization of CNTs by organic materials, doping of CNTs, by catalytic metal nanoparticle/nanocluster as well as metal oxides. Such approached are discussed below.

CNT gas sensors functionalized with organic polymers

Organic polymers in gas sensors react to analytes by changing their physical or chemical properties. Among such polymers having delocalized bonds that make its semiconducting or even highly conductive, polyaniline, polypyrrole, and polythiophene should be mentioned. Amperometric, voltammetric, conductometric and potentiometri sensors of ammonia, nitrogen dioxide, carbon monoxide and VOCs made from such polymers. The conductance changes observed due to modulating the doping level in the conducting polymers upon exposure to analytes. It was showed that non-covalently drop coating of polyethylene mine (PEI) and Nation (a polymeric per fluorinated sulfuric acid monomer) onto SWCNT ChemFETs resulted in gas sensors with improved sensitivity and selectivity for NO_2 and NH_3. SWCNTs from p-type to n-type semiconductors were able to detect less than 1 ppb NO_2 while being insensitive toward NH_3. In contrast to PEI-coated sensors, Nafion coated SWCNTs were insensitive to NO_2 while exhibiting a good sensitivity toward NH_3. PEI-polymer-coated SWCNT ChemFETs had n-type characteristics and were used as CO_2 gas sensors having a high sensitivity, fast response time and complete reversibility for CO_2 concentrations ranging from 500 ppm to 10% in air. The SWCNT-Ethyl cellulose and polymethylmethacrylate sensors are reported, chlorosulfonated polyethylene and hydroxypropyl cellulose are used for detection of Cl2 and HCl. NH_3 sensor made of composite PVP polymer and CNT film shown rather fast response, which did not detected for CNT sensor. Polymer coated SWCNT sensors for detection of dimethyl methylphosphonate were also realized. Synergistic effect in the oxygen and NH_3 gas sensitivity of polypyrrole/SWCNT composites were demonstrated. The modification in polypyrrole results in a synenergistic effect – nanocomposite has ten times more sensitive than sensors made of polypyrrole or SWCNT separately.

Metal nanoparticle/nanocluster functionalized CNT gas sensors

Elemental Pd and Pt are well-known catalysts with high H_2 solubility and diffusivity, as well as good corrosion resistivity. Pd-functionalized SWCNTs shown high sensitivity toward H_2, with a 50% greater sensitivity of up to 50% relative resistance change to 400 ppm H_2 for individual Pd-functionalized SWNTs compared to SWCNT bundles. The response time was 5– 10 s, and the time for recovery was about 400 s. The adsorbed H_2 molecules are dissociated as hydrogen atoms, which dissolve into Pd with a high solubility, leading to a decrease in the work function of Pd. This increases electron transfer from Pd to SWNT and causes a decrease in conductance. The process is reversible.

Gold has been found to be sensitive to odorous gases containing thiol vapor and H_2S. Single wall and multiwall CNTs decorated with different metals (Rh, Ni, Au, Pd, Al, Ag etc.) were proposed for detecting H_2S, CH_4, H_2, CO, O_3, C_2H_5, NO_2, CO_2, CH_4, C_2H_5OH and NH_3. CNTs with comb electrodes can be used to detect gases at low concentrations (e.g. low ppb level). CNTs films coated by Co-catalyst perform chemical detection of NO_2, NH_3, CO_2, CH_4, CO and C_2H_5OH are operated at room temperature. Compared to polymer-based sensors, metal-based sensors are mechanically and chemically robust and stable, and can operate at higher temperatures and in harsher environments.

Review of previous papers

Some thin or thick films of metal oxides show a fast response to varying gas atmospheres, and they are appropriate for gas sensing systems. Different gas, smoke and ion-selective sensors were investigated and developed by us at Yerevan State University. Gas sensors were made from Bi_2O_3, SnO_2, ZnO, TiO_2, In_2O_3, Ga_2O_3, Fe_2O_3 thin films and other ceramic materials as well as porous silicon. Earlier we developed their theoretical basis and realized gas sensors practically without pre-heating of work body of the sensor. For example, in the case of sensors made of Bi_2O_3, $NaBiTi_2O_6$, $LaAlO_3$-$CaTiO_3$, $Fe_2O_3$and $Bi_2V_4O_{11}$ operating temperature was equal to 20-70°C. Such sensors were sensitive to smoke, ethanol and sulphur vapors as well as to humidity. Our Bi_2O_3 smoke detectors are competitive with photoelectric (optical) and ionization detectors of smoke, which currently can be widely used in fire-alarm systems. Independent testing of our adsorptive type smoke detectors in the USA yielded promising results. We also investigated different metal oxide photoelectrodes for photo-electrochemical conversion of solar energy.

There are several commercial products now, especially made of tin dioxide. These types of sensors continue to suffer of high pre-heating temperature of work body of the sensor, i. e. high consumption of energy, lack of selectivity and long-term stability which limits their applications. Usually SnO_2 sensors do not perform well at room temperature. The range of their operating temperatures spans from 200 to 500 °C. For example, the sensor for O_3 gas showed the most effective at 350 C. Many commercial SnO_2-based sensor devices have been realized to detect organic compounds and hazardous gases (e.g., CO and NO). These gas sensors often operate at high temperatures up to 400 C. Note that existing platinum wire sensors need also in its heating above 400°C and very high cost.

The main problem today is to develop new semiconductor gas sensors working at or near room temperature of work body. In addition, they should be small, cheap and easy to be inserted into microelectronic integral circuits. We report below shortly results of our investigations of metal oxide and CNT sensors were carried out recently with the aim to decrease the temperature of their work body. Physical and gas-sensing behavior of semiconductor sensors depends directly on their preparation methods and conditions. One of the main objectives for research at YSU is to develop nanoparticles, because decreasing in the particle size raises the effective surface area for gas adsorption. The nanosized particles, porosity of the films, and the large surface/ volume ratio ensure high sensitivity. Below a certain critical nano-crystallite size, the sensitivity of the gas sensor increases sharply. This occurs when the nano-crystallite size becomes comparable with the double space-charge layer thickness of the semiconductors under consideration. For nano-crystalline SnO_2 thin film or powder, the calculated value of the space-charge layer thickness is ≈ 3 nm. Our efforts were mainly focused on developing and improving the nanocrystalline SnO_2 processing technique. We studied the response of sensors to detect the presence of H_2 in air at various temperatures (25-300°C). As a result, the maximal response is registered in the 80-130°C range of operating temperatures; although rather high sensitivity to H_2 gas at room temperatures was observed.

Gas sensors made from metal oxides doped with metal cations

Several studies have been focused on doping the SnO_2 matrix to increase the sensitivity of the resulting sensors. Introduction of transitional metal cations into an oxide matrix leads to an increase in surface states, active sites and free carriers, which is important for gas sensor application. For example, the addition of Nb into TiO_2 enhanced the response to CO as it induces the formation of new electronic states, due to its donor-type behavior. Vanadium doped with tin dioxides has a higher response towards SO_2 gas, because of their redox activity for SO_2 oxidation to SO_3. Doping with CuO, MoO_3 and Fe_2O_3 leads to lowering of the work body pre-heating temperature of a sensor and increasing in gas response. Vanadium cations serve as reducible catalytic centers to promote oxidation reactions and enhance O_2 consumption. It is known also that dispersed V–O-support structure adsorbs CO gas at ambient temperature.

Metal oxide-CNT gas sensors

Gas sensors can be realized on the base of SnO_2/CNTs, TiO_2/CNTs, Fe_2O_3/ CNT, WO_3/CNT and Co_3O_4/CNT composite. Using mixed SnO_2 nanoparticles with 1 wt. % MWCNTs (100:1) sensing materials, gas sensors were fabricated on micro platforms made of thick SiN_x membrane. The sensing materials were prepared by mixing SnO_2 nanoparticles and MWCNTs with polymer vehicles to form paste. Such sensors were characterized to NO_2, NH_3 and xylene gases, respectively, as a function of temperature from 180°C to 380°C. It was found that 220°C was the optimum temperature to have the best sensitivities.

We used a MWCNT membrane prepared at Yerevan State and/or Szeged (Hungary) Universities for the manufacture of the nanocomposite SnO_2/MWCNT thin film gas sensors by the sol–gel method. Surface modification of the CNTs/metal-oxide hybrid gas sensors with noble metals (Pt, Pd, Au, Ru, and Rh) promotes an improvement of the gas sensors sensitivity and selectivity because of these metals or its oxides are the catalysts for chemical reactions taking place on the surface. The increase in the electrons concentration in the semiconductor conduction band leads to the reduction of structure resistance in the case of the detection of reducing gases.

It is known also that ruthenium stimulates an increase in the rate of oxidation and other surface reactions, involving adsorption of oxygen from the air on the structure surface which causes an increase in the depletion layer of semiconductor near surface region and hence leads to the enhancement of the sensor response. Our investigations have shown that high response appears only after sensibilization of the MWCNT/SnO_2 tablets in 0.01 and 0.03 $Ru(OH)Cl_3$ water solution. Changes in the sensor resistance were registered at operating temperature 100-350°C. For example, sensors made of the MWCNT/SnO_2/Pd tablets sensitized with 0.03 M Ru (OH) Cl3 solution during 20 min demonstrated rather high response to hydrogen and isobutane already at 120 °C. The resistance of the sensor work body (~700 kOhm) decreased 10 times in ~10 and ~30 s after the injection of isobutane and hydrogen, respectively. Unfortunately, sensors recovered rather badly at this temperature. The recovery time for this sensor was equal ~30 and 15 min after a loss of, respectively, isobutane and hydrogen supply at 120 °C.

Gas i-butane is widely used for domestic purposes, in the cooling plant, and as a fuel, being a part of LPG. Vapors of this gas are hazardous to the human health. Therefore the detection of isobutene vapors in the environment is an important problem. Note that we did not detect i-butane by our sensors made of pure SnO_2 and pure CNTs. But we convinced that the response and selectivity of sensors made of a nanocomposite consisting both non-functionalized CNT and inorganic nanoparticle like SnO_2, ZnO or another metal oxide are dramatically increased. In such hybrid sensors we realized some synenergistic results. The measurements of the sensor response to isobutane at higher temperatures have shown that characteristics become more stable. The sensor reaches the equilibrium state faster, the recovery time decreases down to ~10 min. The sensor response increases with the increase in temperature. The sensors made of the MWCNT/SnO2 nanocomposite sensitized with the 0.03 M Ru (OH) Cl3 solution were the most sensitive ones. However, the response time was anyway lower for the samples, sensitized in the 0.01 M Ru (OH) Cl3 solution. For these sensors, it was equal to ~30–40 s while the response time for the samples sensitized in the 0.03 M Ru (OH) Cl3 solution was equal to ~2–3 min. A limitation of the sensor is its slow recovery after the gas supply is stopped. The prepared sensors made of nanocomposite MWCNT/SnO_2/Pd and sensitized with ruthenium were maintained in the environment of isobutane gas for 24 h with the aim of improving the sensor characteristics. Despite some reduction in the response, it has led to faster sensor recovery (the recovery time decreased down to 2–3 min). In order to improve characteristics, the second annealing after a sensitization with ruthenium was carried out at higher temperatures (650 C and 850 C). The dependence of the response on the concentration of isobutane is almost linear for the MWCNT/SnO_2/Pd sensors. For them, almost the same times of response and recovery were observed. They are equal ~30–40 s at low concentrations of the gas. Note that parameters of these structures remained stable at a rather long-term testing of sensors. The sensitization of MWCNT/SnO_2 nanocomposite with Ru catalyst leads to sharp rise in response to methanol and ethanol vapor up to 10^3 and higher. At that, the cross-sensitivity to other gases decreases. The response to methanol and ethanol vapors appears at the operating temperature of 200°C and decreases exponentially with temperature rise up to 300°C. Such a fictionalization with Ru leads to appreciable increase in response to i-butane. It is observed beginning from gas concentration 50 ppm. The typical response and recovery times of such i-butane sensors at operating temperature of 200 C are 5–7 s and about one minute, respectively. The increase in operating temperature up to 250 C leads to sharp decrease in both response and recovery times down to 1–2 s and 10 s, respectively. The sensitivity remains practically the same; therefore if priority is given to faster response behavior, slightly elevated 250°C operating temperature can be selected. With the following increase in operating temperature (≥300°C), adsorbed oxygen desorbs increasingly from the surface. As a result, the response to i-butane sharply decreases. The surface-ruthenated nanocomposite containing large amount of SnO_2 (1:50) nanocrystallites show high response both to methanol and ethanol vapors. Simultaneously, relatively high response to i-butane is also observed. Approximately the same sensitivity to alcohols (about 10^4) remains at the 1:8 ratios of the nanocomposite components but the response to i-butane sharply decreases. The responses to hydrogen and i-butane disappear completely with the following decreasing of SnO_2 part in the nanocomposite (at 1:4 weight ratios of the components).

Thick-film VOCs sensors based on reheated multi-walled carbon nanotubes coated with tin-dioxide nanoparticle nanocomposite structures (MWCNTs/SnO_2) shown that the optimal conditions for applications as acetone, toluene, ethanol and methanol vapors sensors in view of high response and selectivity relative to each other depend on choice of material synthesis method, mass ratio of the nanocomposite components and selected operating temperature. MWCNTs/SnO_2 sensor structures having the mass ratio of the components 1:4 and 1:24 exhibit selective sensitivity to acetone and toluene vapors at 150°C operating temperature, respectively.

With increase in operating temperature, the response to acetone vapor raises up to 360.4 value at достаточно высокой while the selectivity remains sufficiently high. The largest response to acetone vapors (R_a/R_g 555.62) in steady-state regime (formed after the first acetone vapor influence) is fixed for the set of samples with 1:200 mass ratio of the components to 1000 ppm acetone vapors exposure at 250°C operating temperature. Response and recovery times of these sensors are about 22 and 27 s, respectively.

Thin film ethanol sensors made from α-Fe_2O_3 decorated with MWCNTs (25:1 weight ratios) shown good response to ethanol vapors already at work body temperature of 150°. One dimensional (1D) coaxial nanotubes of Fe_2O_3 based on carbon nanotubes (CNT-Fe_2O_3) were synthesized via atomic layer deposition using ferrocene and oxygen as precursors. CNTs were suitable for such system only if they were chemically functionalized. Nitrogen-doped CNTs (N-CNTs) contributed atomic layer deposition-Fe_2O_3, and various 1D heterostructural coaxial nanotubes were obtained with well-controlled growth of Fe_2O_3 on N-CNTs. Such heterostructural coaxial nanotubes of CNT-Fe_2O_3 may find great potential applications in photocatalysis, gas-sensing, and magnetic fields. $Co_{3-x}Ni_xFe_2O_4$/MWCNT nanocomposite (x = 0.2, 0.4, 0.5, 0.6, 0.8) were synthesized via an in situ solvothermal method using ethylene glycol as solvent. Such nanocomposites have a high selectivity for ammonia. A composite film of cobalt oxide nanosheet and carbon nanotube adsorbs or desorbs CO gas. The adsorption of a small quantity of CO leads to a dramatic change of the CNT conductivity. Therefore, CNT are suited to detect species at low concentrations (e.g. low ppb level). Such a micro carbon monoxide sensor integrated with a readout circuit on chip manufactured by the commercial 0.35 μm complementary metal oxide semiconductor process and a post-process. The readout circuit is used to convert the resistance of the sensor into the voltage output. The post-process of the sensor includes etching the sacrificial layers and coating the sensing film. The advantages of the sensor include work at room temperature, short response/recovery times and easy post process. Experimental results show that the sensitivity of the CO sensor is about 0.19 34 mV/ppm, and the response and recovery times are 23 sec and 34 sec at 200 ppm CO, respectively. Nano-composite structures made from cobalt oxide and SWCNTs for a gas sensor application (NO_x and H_2) show a response of ~200% upon exposure to 4% H2 at room temperature. CuO/ MWNT thin film based ethanol-sensors had maximal sensing response at an operating temperature near 400 °C.

Gas sensors have fabricated based on non-doped and 1 wt% MWCNT-doped tungsten oxide (WO_3) thin films using the powder mixing and electron beam evaporation technique. Hydrogen sensing properties of the thin films have been investigated at gas concentrations ranging from 100 ppm to 50,000 ppm. The results indicate that the MWCNT-doped WO_3 thin film exhibits high sensitivity and selectivity to hydrogen at reduced operating temperatures.

Room Temperature Sensors

Above reported composite sensors still operate at rather high temperatures. Only several authors detected several gases using metal oxide-CNT sensors operated without pre-heating of work body. As it will shown below, such sensors had much better response and shorter response-recovery time, compared to those of sensors made from metal oxide (for example, SnO_2) or CNT material alone.

A SnO_2/MWCNT composite-based NH_3 sensor working at room temperature was fabricated by standard thin film microelectronic technique using both MWCNTs and nanosized SnO_2. At room temperature, the optimal composite sensor exhibited much higher response and faster response-recovery (less than 5 min) to NH_3 gas of concentrations ranging from 60 to 800 ppm, in comparison with the CNT-based NH_3 sensor. 10 wt% MWCNTs/SnO_2 composite was calcined at 500 °C in vacuum of 10^{-2} Torr. As expected, the resistance of the sensor increases upon exposure to electron donating gas NH_3.

An increase in the sensor resistance can be hypothesized that the composite sensing layer behaves as a p-type semiconductor. Probably, the response of the composite sensor should be mainly contributed by the MWCNTs, which have been well known to behave as a p-type semiconductor. Comparing with the CNTs-based NH_3 sensor and the SnO_2-based NH_3 sensor reported previously, as-synthesized composites SnO_2/MWCNTs-based sensors have a higher response to NH_3 gas at room temperature.

Gas sensors made from doped-CNT/SnO_2 composites for NO_2 detection at room temperature were reported. Incorporation of CNTs to a SnO_2 matrix results in a dramatic increase in sensor response at very low operating temperatures and even at room temperature. Probably, the main reason for such response enhancement is the co-existence of two different depletion

layers (and associated potential barriers): one at the surface of the metal oxide grains and the other one at the interface between MWCNT and metal oxide. Nitrogen or boron doped CNTs were added into a SnO_2 matrix, which enhances the nanotube conductivity. Such a hybrid sensor was prepared to detect low ppb concentrations of NO_2 in air and shown at least 10 times higher response towards NO_2 at room temperature in comparison with the pristine SnO_2 and N or B-substituted CNT sensors. Nitrogen doped MWNTs sensors exhibited response and recovery times of the order of a few seconds.

It was also established that sensors based on pure tin oxide nanoparticles and on pure plasma treated CNTs did not show responsiveness to nitrogen dioxide and carbon monoxide. In contrast, sensors made of SnO_2-decorated plasma treated CNTs are gas sensitive soon at room temperature. Response time to 1ppm NO_2 was 4 and 3min when sensors are operated at room temperature and 150 C, respectively.

Sensors made of the mixture of an intermediate amount of tin dioxide precursor (i.e., 20 ml)with 12mg of oxygen plasma treated MWCNTs were also sensitive to CO. However, CO responsiveness was far lower than the one for NO_2. Response time was 5min for 2ppm of CO. Such sensors showed a decrease in resistance with exposure to CO when operated at room temperature. This experimental result is qualitatively consistent with what has been observed. All these research teams have attributed such behavior to the decrease in the work function of SnO_2 in the presence of CO and a decrease in sensor resistance.

The Co_3O_4–SnO_2 material was used. Its maximum sensor response to CO in the working temperature range from 25 to 150 C was found at 25 C. Doping 0.1% CNT into Co_3O_4–SnO_2 enhanced the CO response of non-doped Co_3O_4–SnO_2. The sensor response varied under CO concentrations ranging from 20 to 1000 ppm.

Pt-doped TiO_2/MWCNT composites have been synthesized by a sol–gel approach, characterized and tested as sensing layer in resistive devices. Regardless the nominal C/Ti molar ratio, only the anatase phase of titania is formed. It was established that the TiO_2/MWCNT composite samples with nominal C/Ti molar ratio ranging from 3.6 to 17.0 were the best. Hydrogen monitoring takes place only with the Pt/TiO_2/ MWCNT ternary sensor, suggesting a synergic action among metal oxide, noble metal and CNTs. Pt acts as a catalytic additive in the Pt-TiO_2/MWNT-based sensors which were found to be sensitive to hydrogen at concentrations between 0.5 and 3% in air. They can be used as hydrogen leak detection devices.

It is possible to make sensors on the base of SWCNTs. SnO_2/arc-discharge SWCNT hybrid material based sensor was also developed for the detection of NH_3 and O_3 at room temperature. Sol gel and dip coating techniques was used for preparation of the hybrid sensor which also had an enhanced sensitivity as compared to pure SnO_2 or pure SWNTs based sensor. The detection limit at room temperature was lower than 20 ppb for NH_3 and O_3, respectively. The fast response (few minutes) and a full recovery at room temperature were detected. The H_2 gas sensor was on the base of nanocomposite Co_3O_4 nanocrystals/ SWCNT which is working up to 4% H_2 at room temperature.

On mechanism of response of functionalized sensors to gases

It is obvious today that the doping of metal oxide with CNTs leads to better sensitivity and lower work body temperature of such a hybrid sensor. Several processes take place in such nanocomposites. The full picture of complicate phenomena is not possible to propose today, but we have to take into account the following reasons:

MWCNTs have a huge specific surface area and a nanoscale structure, which exposes a large number of sites at which the gases can react. Detection of various gases can be realized at low temperatures of pre-heating of work body of sensor. Electric conductivity of CNTs is much higher in comparison with the conductivity of metal oxides that can be used to increase the sensitivity of the micro-gas sensors. The CNTs play mostly a role in reducing the resistance of the sensing material. The metal oxide nanoparticles mainly control the sensing properties. Since metal oxide film has mainly n-type semiconductor characteristics and MWCNTs have p-type, there are two different depletion regions in these hybrid films. Note that the first depletion region is located at the metal oxide surface and the second one is located in the interface between the metal oxide nanoparticles and the MWCNTs.

Creation of nanochannels and formation of p-n or heterojunctions leads to an enhanced gas sensitivity of such a hybridized gas sensor as the change in barrier height or in the conductivity of the metal oxide sensitive layer may modulate the depletion layer at the p-n junction. Latter may cause the improvement in the performance of the gas sensor at low operating temperature.

The higher is the CNTs content the major conducting carriers are in nanostructure. For example, when the MWCNTs/SnO composites are exposed to NH_3 gas, NH_3 molecules may interact with the MWCNTs by replacing the pre-adsorbed oxygen resulting in oxidation of NH_3 gas at the surface and removing the oxygen accordingly. Therefore, the potential barrier of the hetero-junction formed by MWCNTs and SnO_2 can be modulated and the conductivity of the composite material during the exposure to NH3 gas can be changed.

Apparently, discussed possible mechanisms require further experimental and theoretical investigations. Beside, the response of the composite thin film gas sensor strongly depends on the preparation process of the sensitive film. For example if the composite thin film with the MWCNTs content of 15 wt%, the MWCNTs diameter of 60–100 nm, the calcination

temperature of 530 °C under vacuum of 10^{-2} Torr, the film thickness of 400 nm is optimal. This result also implies that these conditions need to be optimized for practical applications of the composites of semiconductor metal oxide/carbon.

Conclusion

1. Use of pristine CNT as sensors does not promising.
2. Functionalization of CNTs can be made with organic materials. Hyper sensibility and selectivity of detection of CO_2, NH_3, O_2, Cl_2, HCl, dimetyldimetylphosphate observed by CNT nanocomposites covered with polyethylene, polyanylyne and polypyrrol.
3. CNTs, decorated with Pd, Rh, Au and Ni nanoparticles are suggested for detection of H_2S, CH_4, H_2, CO, O_2, C_6H_6, NH_3, NO_2, and C2H5OH up to their ppb level.
4. Special interest is attended to investigation of possibilities of manufacture of CNT functionalized (decorated) with different metal oxide composites. Most of its are carried out by CNT, decorated with SnO_2. Modifications of such nanosensors surface with precious metals led to remarkable improve of the sensitivity and selectivity of sensors.
5. Sensibilisation of CNT- SnO_2 composites in water solutions of Ru(OH)Cl3 leads to high response to hydrogen as well as to synenergistic effect during detection of isobutene and the lowering of temperature of pre-heating of work body of sensors up to 150-200^{0}C. Such sensors are sensitive also to vapors of VOC gases (acetone, toluene, ethanol and methanol) at approving the same temperatures of pre-heating.
6. Thin film (including 1D film) nanosensors of ethanol vapors were manufactured on the base of CNT-Fe_2O_3 solid solutions. Sensors of H_2, NO_x and CO were manufactured from CNTs with cobalt oxide, $Co_{1-x}Ni_xFe_2O_4$, CuO and WO_3.
7. Substantial interest invokes research and development of nanosensors working without pre-heating of their work body (at room tmperature). 10^0a- SnO_2 –CNT nanocomposit sensor detected ammonia and NO_2. Doping of CNT with N and B and its synthesis with metal oxide SnO2 allowed dramatically increase the conductivity of the nanosensor and response to CO and NO_2. Nanosensors made from Co_3O_4- SnO_2 and Pt-TiO_2 CNT was sensitive to H_2, NH_3 and O_3 on the 20 ppb level of gas concentration.
8. Nanosensors made from all mentioned composites CNT-metal oxides had lowest response and shorter times.
9. It is clear that the doping of metal oxides with CNTs lead to greater sensitivity to gases, better speed to response of nanosensors and a lowering of temperature of pre-heating of their work body (up to room temperature, when the pre-heating is not necessary). Possible mechanisms of the response of developed sensors to gases are discussed. Doubtless, that different type of conductivity of CNTs and metaloxides, change in the work function (higth of potential barrier), modulation of formed heterujunctions should be take into account at the analysis of complicate processes and phenomena in gas sensitive structures reported above.

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