Sensing Environmental Contaminants Using Carbon Nanofibers Doped Tin-Oxide Composites

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Enhanced urbanization and industrialization has necessitated use of distributed miniaturized sensors for persistent observation of gases and various other contaminants that may be harmful to our well-being. Several metal oxide viz., SnO_2, ZnO, TiO_2, WO_2, Ga_2O_3, are examined for gas sensing applications for environmental contaminants with applications ranging from monitoring of industrial emission processes to heavily populated urban settings. In the present study, the objective is to investigate bulk sensors via ceramic processing of nanoparticles of several oxides reinforced with carbon nanofibers (CNFs) and WO_3. The composites are subjected to different pressing pressures and changes in their sensing/detection characteristics is evaluated by their response to different concentrations of ethyl alcohol. It is observed that the sensitivity of SnO_2/CNF sensors for ethyl alcohol increased by almost two fold as compared to that of SnO_2 8-ton pressed sensor with lower response time.

Keywords: gas sensors, ceramic processing, oxides, nanoparticles, response time.

УДК 66

1. INTRODUCTION

With ever increasing population, coupled with urbanization and industrialization, monitoring emission from industrial processes and environmental sensing in large cities is vital towards environmental sustainability. The omnipresence of sensors in the transportation sector, industrial automation and residential architecture has further contributed to safety, security, and sustainability. From a liability standpoint, workers in a production environment face the threat of injury or death, should they be exposed to toxic vapors or gasses. Furthermore, the fabrication processes used for various types of devices, equipment and systems themselves require careful selection of environmental friendly products and treating emission by-products to minimize environmental impact. Such efforts require accurate, durable, reliable, and fast chemical sensors to mitigate and decrease these risks.

Gas sensors based on wide band semiconductor metal oxides play an important role in the detection of toxic pollutants (CO, H_2S, NO_x, SO_2) and combustible gases (H_2, CH_4 and flammable organic vapors, etc.) [1]. Metal oxide materials, such as SnO_2, ZnO, TiO_2, WO_2, Ga_2O_3, and others, have recently been examined for gas sensing applications and for the control of industrial processes. Recently, monitoring of pollutant gaseous species such as aromatic hydrocarbons, oxides of nitrogen (NO_x), carbon monoxide (CO), ozone, etc. emitted by the automotive exhausts, has received a great deal of attention. Research efforts aiming to develop innovative monitoring systems for the detection and measuring sub-parts per million concentrations of these gases have been undertaken [2]. To substitute the standard analytical tools with a new generation of detectors, different approaches have been followed. In recent years semiconductor gas sensors based metal oxide have become a well establishes component of the technology available for monitoring atmospheric composition. The advantages range from good sensitivity to some relevant gases like CO, H_2, NO_x and hydrocarbon, simple signal processing, low production cost and small size. Semiconductor metal oxides sensors play a crucial role in the detection of toxic pollutants (CO, H_2S, NO_x, SO_2, etc.), gas leakage detection such as propane, butane and combustible gases (H_2, CH_4 and flammable organic vapors, etc.) owing to their advantages of robust nature, reduced sensitivity to moisture and temperature influence, simple electronic interface, quick response and recovery time [1]. Tin oxide (SnO_2) is one of the most extensively studied metal oxide materials [1, 3]. The key issues are (a) sensitivity, (b) selectivity to the specific gas, (c) insensitivity to moisture, and (d) low power consumption. As is seen below in Table, one can conclude that analytical instruments offer an expensive option as compared to gas sensors, coupled by a size that makes it difficult to deploy in field applications. Solid state sensors offer excellent alternatives for implementing environmental monitoring due to their light weight, extremely small size and ease by which they can be installed almost anywhere so as to receive data that can eventually be transmitted through a Wireless geographic information system (GIS) network system to the general public.

Table. Comparison between analytical instruments and gas sensors

Characteristics	Analytical instruments	Gas sensor
Resolution	Excellent	Comparable
Cost	Very high	Reasonable
Size	Bulky (factory)	Compact
Rigidity	Fragile	Rigid (replaceable)
Process control	Difficult	Compatible
Volume production	Difficult	Moderate
Measurement Mode	Instantaneous	Continuous (real-time)

Various techniques have been developed to improve the sensitivity and selectivity of these sensors. A large part of the literature deals with characterization of sensors employing different forms of oxides, the effect of catalytic or other additives or ion implantation, use of masks and filters to improve selectivity and temperature programming techniques etc. [3]. However, a lack of consistency in sensor properties has been a major problem associated with various techniques used for the fabrication of sensors.

Bulk, thick, and thin films of SnO_2 have been used in the fabrication of gas sensors. Thin-film sensors are of great interest because of relatively small geometry, low power consumption, and sharp sensing effect, among others. A thin film sensor having a thickness of less than a few hundred nanometers has reasonably good sensitivity but usually shows poor stability due to weak mechanical strength. The dispersions of dopants, which enhances the sensitivity of thin films is not as satisfactory as those used for thick or bulk type sensors [4–6]. For thick-film or bulk type sensor, dopants (or additives) are usually mixed homogeneously with the powder precursors. Recently, it has been reported that composite sensors incorporating differing proportions of tin oxide and zinc oxide exhibit higher sensitivity over a range of organic vapors [7]. The general mechanism for a metal oxide sensor is a change in the resistance (or conductance) of the sensor when it is exposed to pollutant gas, relative to the sensor resistance in background air. The sensor resistance in most cases is determined at a constant operation temperature and by DC-measurement. Generally, the depletion zone at the surface of metal oxide sensor is present due to absorption of the atmospheric oxygen. When the metal oxide sensor absorbs a reducing gas, the depletion area at the surface decreases thus increasing conductivity. On the contrary, if a metal oxide sensor absorbs an oxidizing gas, the depletion zone at the surface increases thus decreasing conductivity. Hence, a change of conductivity or resistance is dependent on gas concentration. A change in resistance is caused by a loss or a gain of surface electrons as a result of adsorbed oxygen reacting with the target gas. If an oxide is an *n*-type then there is either a donor (reducing gas) or acceptor (oxidizing gas) of electrons from the conduction band. The result is that *n*-type oxides increase their resistance when oxidizing gases such as NO_x, O_3 are present while reducing gases such as CO, CH_4, lead to a reduction in resistance. The opposite is valid for *p*-type oxides, such as Cr_2TiO_3, where electron exchange due to gas interaction leads either to an increase (oxidizing gas) or decrease (reducing gas) in holes in the valence band.

Composite sensors have a significantly higher sensitivity than sensors fabricated from tin dioxide or zinc oxide, when operated under identical experimental conditions. It has been further proposed that an increase in sensitivity is due to synergistic effects, such as complementary catalytic activity, formation of hetero-junctions and changes in microstructure on sintering [8, 9]. More recently, carbon nanotubes (CNTs) have been employed as active materials in semiconductor gas sensors [10–13]. The potential of CNTs for detecting gases arises from their very large surface area and exceptional electronic properties. However, due to their strong sp^2 bonding in a near perfect hexagonal network, pristine CNTs prevent formation of chemical bonds with most molecules due to their chemically inert nature [11]. The interaction of gas molecules with CNT is understood using density functional theory (DFT) [12] and beyond the scope of this article. There are many factors affecting the gas-sensing properties. Besides the intrinsic factors of materials, some extrinsic factors are grain size, porosity and operating temperature [14].

Our objective of this investigation is limited to the extent of binary bulk sensors via ceramic processing of nanoparticles of tin oxide fabricated under different pressing pressures and reinforced with carbon nanofiber composites for their response in terms of sensitivity and response time to ethyl alcohol. The study was also performed to determine the detection capability of sensors for different concentrations and to propose a possible mechanism for their response mechanisms.

2. EXPERIMENTAL

2.1. Sensor Fabrication

Bulk sensors were fabricated by optimized ceramic processing parameters. Tin (IV) oxide and

tungsten oxide nanopowders (99.9% metals basis, 50 nm, MTI Corp.), and carbon nanofibers (diameter 150 nm, surface are 20–30 m^2/gm, Pyrograf Products, Inc.) were used in the fabrication of the pellets. It is important to mention carbon nanotubes (CNT) and carbon nanofibers (CNF) are both hollow, few nanometers in scale and produced commercially. There are distinct differences which significantly impact their performance for sensors processing. The primary differences between the materials are morphology, size, ease of processing, and low-cost. Carbon nanofibers, also known as Stacked-Cup Carbon Nanotubes (SCCNT), have a unique morphology in that graphene planes are canted from the fiber axis resulting in exposed edge planes on the interior and exterior surfaces of the fiber. CNTs, on the other hand, typically resemble an assembly of concentric cylinders of graphene. In each case, tin oxide (S)/tungsten oxide (W) mixtures were ground, milled and then pressed under 4T, 6T, 8T and 10T to form pellets, thereafter named as ST4 (viz. tin oxide under 4T), ST6, ST8 and ST10, 16SW4 (1.6g + 0.4g) and 18SW2 (1.8g + 0.2g), respectively. For the fabrication of nanocomposites, 0.01 gram of CNF were added to 2 grams of tin oxide mixtures and pressed under 8T of pressure to form pellets of 14 mm diameter and 2 mm thickness, thereafter named as SCNF. The pellets were subjected to a thermal profile which started with a heating ramp rate of 2ºC/min to 500ºC and kept at this temperature for 2 hrs and then heated at the rate of 5ºC/min to a sintering temperature of 1000ºC for 2 hrs in ambient air. Then pellets were cooled down to room temperature at the rate of approximately 1ºC/min. Contacts/electrodes were painted on with Silver paste on the same surface with a finite gap of about 3 mm as depicted in Figure 1.

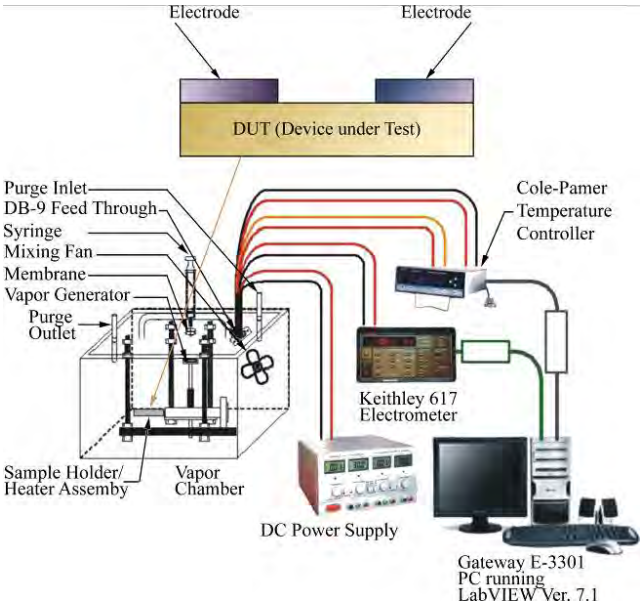

Fig. 1. A design of chemical sensor.

2.2. Vapor Measurement System

Gas sensing properties were investigated under static conditions in a sensor testing system in a chamber of 5.2 liters. The test fixture is described elsewhere [15]. The output resistance variations of the sensor were measured simultaneously with respect to temperature and for time of injection of propanol. The output-resistance was recorded using a Keithley 617 programmable electrometer connected to a computer. The resistance variation was measured for different concentrations of test vapors (ethyl alcohol) ranging from 50 µL to 450 µL injected consecutively at appropriate time intervals. The sensors were fixed onto a sample holder and the operating temperature of the film was determined with a thermocouple attached to the sensor. Sensitivity was calculated using the following formula:

$$\text{Sensitivity } (S) = R_0/R.$$

Where R is the sensor resistance influenced by the isopropanol vapors, and R_0 is the sensor resistance in the ambient air.

3. RESULTS AND DISCUSSION

Figure 2 shows the SEM of sensor pellet ST10. SEM picture of the sample of ST10 has predominately rectangular but rounded crystalline structures of various sizes ranging from 50–100 nm. It can be inferred from the micrograph and resolution scale that the sintered samples have nanostructured surface morphologies and roughness comparable to constituent carbon nanotubes/fibers. Figure 3 shows the response of various sensors with 500 µL injected ethyl alcohol. Figure 4 shows the response of the sensors with 50 µL injected ethyl alcohol. Figure 5 and Figure 6 illustrate the response as a function of ethyl alcohol concentration of ST8 and SCNF sensors.

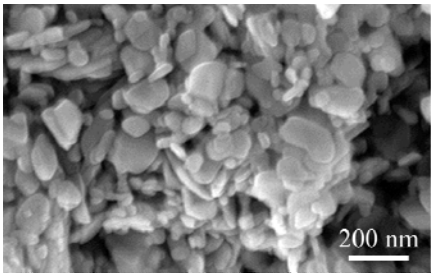

Fig. 2. SEM picture of sensor pellet ST10.

There is an increase of sensitivity with an increase of injected concentration of vapors. ST8 shows the highest sensitivity among the strongly pressed sensors. SCNF sensors show the highest sensitivity among all sensors investigated. The sensitivity increases with concentration of injected propanol. With a fixed surface area, a lower concentration of gas implies a lower coverage of gas molecu-

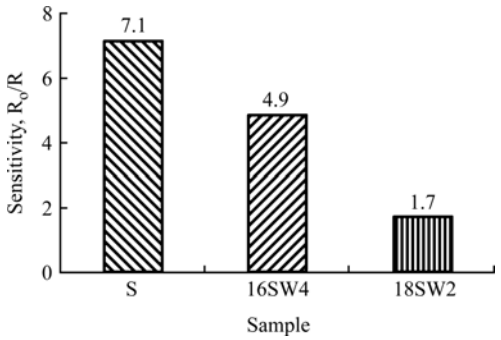

Fig. 3. Sensitivity (R_0/R) at t_{20} of the various sensor pellets to 500 μL ethyl alcohol displayed in the bar chart.

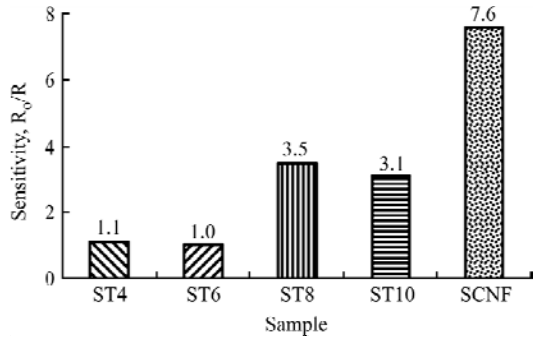

Fig. 4. Sensitivity (R_0/R) at t_{20} of the various sensor pellets to 50 μL ethyl alcohol displayed in the bar chart [21].

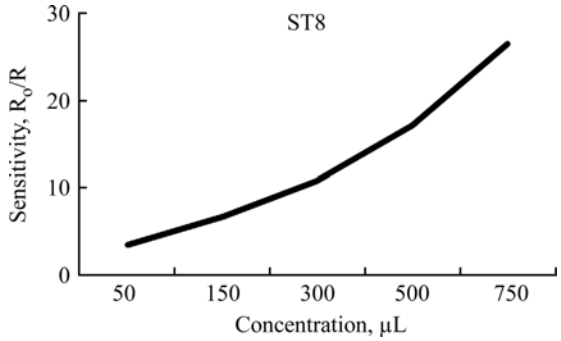

Fig. 5. Sensitivity of ST8 sensor to ethyl alcohol concentration levels using static method.

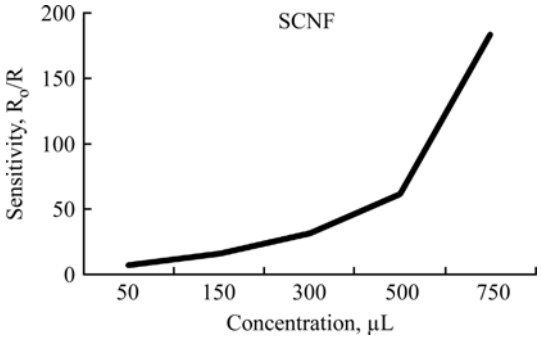

Fig. 6. Sensitivity of SCNF sensor to ethyl alcohol concentration levels using static method [21].

les on the surface. An increase in vapor concentration raises the surface coverage and thus increases the observed sensitivity. The response time of 50 μL ethyl alcohol vapors was found to be lower for SCNF (13.6 min.) than ST8 (15 min) sensor. Based on the results, SCNF sensor shows the outstanding sensitivity and response time.

A proposed mechanism for detection of isopropanol vapors is to use the non-stoichiometric structure of SnO_2 which have free electrons originating from oxygen vacancies that contribute to conductivity (*n*-type). The mechanism can be described by the following equation:

$$O_0 \text{ (bulk)} = V_0 + 2e^- + \tfrac{1}{2}O_2 \text{ (gas)}. \quad (1)$$

Thus in an *n*-type metal-oxide semiconductor, the conduction electrons (e^-) come primarily from point defects (oxygen vacancies and interstitial tin atoms) and play a major role in the gas sensing operation [1, 3, 16] which is the combination of two adsorption reactions. So, the reaction sequences on ethyl alcohol, $(CH_3)\,CH_2OH$, can be written in the following reaction steps with physical and chemical adsorption:

Step I for sensitizing reaction:

$$O_2(\text{gas}) + 2e^- \rightarrow 2O^- + \Delta H_1. \quad (2)$$

Step II for detection reaction:

$$(CH_3)CH_2OH + O^- + \Delta H_2 \rightarrow \rightarrow e^- + CH_2COCH_2 + H_2O + \Delta H_3. \quad (3)$$

Surface morphology of the films is an important issue because a smaller grain size yields a larger specific surface area which results in greater adsorption and higher sensitivity [17, 18]. The mechanisms for increase in response in CNF-SnO_2 composite can be explained via the formation of (*n*-oxide)/(*p*-CNF)/(*n*-oxide) hetero-junctions. When tin oxide (*n*-oxide) is exposed to propanol gas, the gas molecules will react with oxygen ions previously adsorbed on the surface as depicted in step II which releases electrons and increases the conductivity of sensing material. It is worth mentioning that *n*-type tin oxide and *p*-type CNF form a hetero-structure like that of the working principle of an *n-p-n* amplifier. CNF acts like a base with blocked electrons transferring from an *n* (emitter) to *n* (collector) thus lowering the barrier a little bit which allows a large amount of electrons to pass from emitter to collector [12]. Thus, this amplification effect can explain the improvement in gas sensor performance of CNF-SnO_2 as compared with other investigated tin oxide based sensor pellets. Changes in sensor response of ST4, ST6, ST8, ST10, 16SW4 and 18SW2 pellet sensors can be explained by investigating the measurement of pore size distributions. Observed changes in the sensitivity of sensor elements can be attributed to porosity and particle size variation. A decrease in the number of pores is likely to be responsible for a decrease in sensor response [19-21] as highly porous sensors have high sensitivity.

4. CONCLUSIONS

For this investigation, we prepared and characterized gas sensors for the detection of ethyl alcohol. It was experimentally demonstrated that a tin oxide sensor reinforced with carbon nanofibers yielded improved gas-sensing properties with faster response

times as compared to regular tin oxide sensors. The gas-sensing mechanism of a nano-composite sensor is proposed to be a formation of (*n*-oxide)/(*p*-CNF)/(*n*-oxide) hetero-junctions. However, further study is needed via atomic force microscopy to understand higher sensitivity of CNF doped sensors under higher pressure loads. The sensors have potential to be used for geographically dispersed and environmental sensing and internet-of-things (IoT) applications.

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Реферат

Усиленная урбанизация и индустриализация привели к необходимости использовать миниатюрные сенсоры для постоянного мониторинга газов и других загрязнений, которые могут быть вредны для нашего самочувствия. Некоторые металлические окислы, например SnO_2, ZnO, TiO_2, WO_2, Ga_2O_3, исследованы на предмет их применения в качестве газовых сенсоров с применением начиная от мониторинга индустриальных выбросов до мониторинга сильно загрязненных городских районов. В данной работе целью было исследование объемных (массивных) сенсоров приготовленных металлокерамическим методом (спеканием) наночастиц из некоторых оксидов усиленных карбоновыми нано-нитями (CNFs), а также WO_3. Эти композиты были подвергнуты различному давлению, после чего их характеристики чувствительности, были оценены по отклику на различные концентрации этилового спирта. Установлено, что композитные сенсоры SnO_2/CNF обладают вдвое более высокой чувствительностью к этиловому спирту, нежели просто SnO_2 – сенсор, приготовленный прессованием 8-тонным прессом, а также меньшей инерционностью (меньшим временем отклика).

Ключевые слова: газовый сенсор, керамическая технология, оксиды, наночастицы, время отклика.