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Improving Operating Temperature of Gas Sensors by Forming Heterojunctions

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Introduction

Carbon Nanotube (CNT) based gas sensors have a variety of advantages over conventional gas sensors. They are smaller in size, consume less power, have quicker response times, and have great electronic and thermal properties. In addition, they are easy to functionalize and have amazing mechanical properties that allow them to be modified and targeted for a specific gas molecule. This allows them to be highly specific.

The drawbacks of CNT gas sensors are that they have low sensitivity and poor selectivity. CNT based gas sensors need to be functionalized in order to be optimized for detection of certain gas molecules, and once this functionalization is performed, it makes the sensor a poor detector for other gases. Obtaining selectivity would require functionalization with non-optimal functional groups resulting in sub-par sensitivity. The other drawback is that CNTs are required to be of defined structure and property to function properly. This makes their mass-fabrication difficult and often expensive. Figure 1 shows a simple CNT field effect transistor (FET) that can be used to detect gas molecules bound to the functionalized CNT molecules. These gas molecules induce a change in conductance and/or resistance affecting the current passing from source to drain.

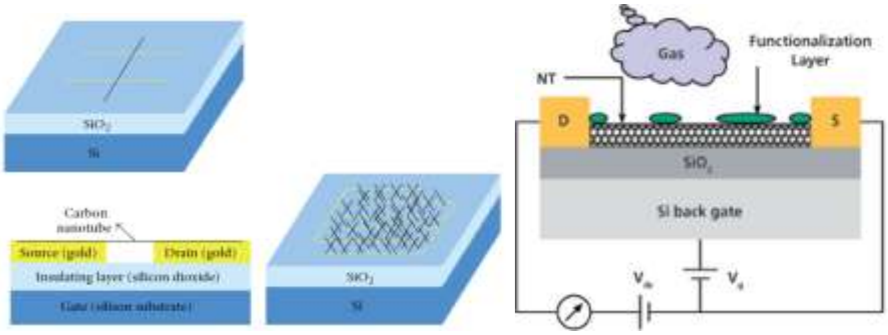

Figure 1 Schematic of a State-of-the-Art CNT Gas Sensor

The most important drawback of CNT-based gas sensors is that they are slow to recover, and most of the time the recovery is incomplete. This requires the sensor to be operated at elevated

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temperatures to facilitate recovery. The rate of desorption of gas molecules from the CNT matrix is given by the following Arrhenius equation:

$$r_d = K' f(\theta) e^{-\frac{E_d}{RT}}$$

This equation makes it clear that the higher the temperature, the higher the rate of desorption r_d. Consequently, these CNT gas sensors need to be exposed to high temperatures to ensure complete and quick recovery so the same sensor can be used to detect the same gas once more or a different gas altogether. However, there is a limit on the maximum desorption rate since there is a cap on the highest temperature the CNT gas sensor can be exposed to owing to the fact that high operating temperatures could burn the CNTs causing severe structural damage.

Metal oxide gas sensors have been investigated significantly over several decades since they have superior response, low cost, and most importantly fast response and recovery times. However, metal oxide based sensors are operated at a temperature range between 200 and 800°C. Such high operating temperatures make pure metal oxide sensors inconvenient to use in space application such as satellites and space shuttles where as much energy must be conserved. Ideally, as little energy of the stored shuttle is used to maintain the operating temperature environment of the array of gas sensors on board leaving as much energy for the operation of the shuttle itself.

This paper describes an improvement that involves the fabrication of a thin-film consisting of a composite material containing modified single-walled carbon nantobes (SWCNT) and metal oxides (MOs) such as tin oxide, strontium oxide, molybdenum oxide, titanium dioxide, or tungsten oxide to help lower the operating temperature of the sensor and still have reasonable recovery times. The following sections explain this composited thin-film in further detail.

Sensor Design

Given the strengths of the two types of gas sensors, namely metal oxide sensors and CNT sensors, it seems prudent to obtain a metal oxide/CNT composite whose combined performance will hopefully be better than any of the individual sensor's performance by eliminating some or all of the drawbacks of each individual type of sensor. Hybrids have proven to be effective in improving the performance of electronic devices in several other applications.

One example of an advanced composite material with improved sensing properties would a SWCNT and SnO_2/TiO_2 nanocomposite. These nanocomposites can be achieved by incorporating SWCNT into a metal oxide substrate to form a film that be used as the sensing element. For example, we could spin coat or drop coat a metallic solution dispersed with SWCNTs to form a composite film. Another example is to synthesize core/shell nanostructures with MWCNTs and metal oxides using a simple wet chemical method. Here MWCNTs would form the core and metal oxide nanoparticles like SnO_2 would form the shell. In this design, the thickness of the shell and the particle-size of the SnO_2 nanoparticles can easily be varied by modifying the wet chemical process. A simple heat treatment or annealing process could then be used to fuse the composite in place for enhanced performance.

In any composite design, the mixture of CNTs and metal oxides would form 3 types of interfaces:

1. Metal oxide – metal oxide interface (grain boundaries)
2. CNT–CNT interface
3. CNT–Metal oxide interface

Due to the presence of these 3 interfaces, we expect that the composite yields an improved electrical transport mechanism. We already know that the resistance of this composite will likely be dominated by the grain boundaries between the metal oxide grains since CNTs have enhanced conductivity properties. Thus the addition of SWCNTs to the metal oxide matrix will allow the formation of “nanopasses” that will significantly help improve conduction within the composite. Thus we expect the electrons from source to drain will largely travel inside the metal oxide grains, but will conduct through the mixed-in SWCNTs with significantly lower resistance.

The key property of the transport model is the formation of a depletion layer at the CNT and metal oxide interface. The CNT can be thought to be a p-type semiconductor with an excess of holes, while the metal oxide can be thought to be an n-type semiconductor with an abundance of electrons. When the composite is formed and annealed, the excess electrons and holes in proximity neutralize one another forming a small depletion region. This depletion region acts as resistance to the transport of electrons within the field-effect transistor (FET). When gases are adsorbed on to the surface of the composite film, the depletion layer will be modulated causing a change in resistance which can be detected.

A few design considerations need to be kept in mind while designing the thin film containing the MWCNT/metal-oxide nanocomposite material. These design considerations are necessary to maintain good electronic conduction in the hybrid material. These design considerations are directly affected by the preparation process and preparation parameters of the thin film. For example, the film thickness t directly affects the response of the sensor. Too large a film thickness would reduce diffusion properties in the film leading to a smaller response. The weight % of MWCNT in the composite matrix is also a crucial design parameter. A weight % from 5%-25% would probably be ideal. But experimentation will need to be done to determine the most ideal composition split. The diameter d of the MWCNTs would also affect the conductive properties of the composite. A larger diameter would allow for more gas molecules to be adsorbed on to the film. The last design parameter worth tweaking is the temperature T that the film is annealed at to fuse the composites together. A high T would ensure a better contact between the metal oxides and the CNTs. However, the anneal temperature cannot be too high for otherwise the CNTs would burn (since they are just carbon) inducing structural damage. Lastly,

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the CNTs can still be functionalized as usual with functional groups such as hydroxyl, oxygen, oxygen plasma, etc.

Expected Performance

We expect a much higher response with a gas sensor fabricated using this novel nanocomposite material as compared to the individual gas sensors due to the superior electron transport characteristics. We also expect quicker recovery times at lower temperatures. This hybrid material will make gases like ammonia (NH_3) bind less tightly to the SWCNT / metal-oxide matrix improving recovery time and allowing for recovery at significantly lower temperatures.

This new gas sensor will enable us to detect important gases such as NO_2, H_2, NH_3, LPG (Liquefied Petroleum Gas), and ethanol at room temperatures – something that was not possible previously. The less-tight binding of these gas molecules to the composite matrix allows for quick desorption even at room temperatures thereby reducing the working temperature of the sensor device.

The new gas sensor will also be more sensitive to reducing molecules. Reducing molecules that are easily oxidized, ie. that easily lose electrons act like n-type dopants when interacting with CNTs. These n-type dopants can act as charge carriers within the depletion regions thereby causing the resistance to decrease noticeably leading to an increase in response.

Summary

In this paper, an improved sensor that combines the strengths of two pre-existing sensors, namely CNT FET gas sensors and metal oxide gas sensors was discussed. This hybrid material can be mixed together in as a bulk composite or as a core/shell nanostructure. The goal is to lower the operating temperature of the gas sensor especially during the desorption phase. This is achieved by superior response characteristics and sensitivity at room temperature and decreasing the binding strength of the gas molecules making them easier to come off the CNTs. This new gas sensor will enable us to detect important gases such as NO2, H2, NH3, LPG, and ethanol at room temperatures – something that was not possible previously.

References

[1] "Carbon Nanotubes As Active Components of Gas Sensors", Wei-De Zhang and Wen-Hui Zhang, *Journal of Sensors*, **2009**, 160698, 2009.