Razi University

Factually of Science

Department of Physics

Ph.D. Thesis

Investigation of gas sensing properties of zigzag single-walled carbon nanotubes and armchair graphene nanoribbons

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Abstract

The main purpose of this thesis is the investigation of the gas sensing properties of zigzag carbon nanotubes and armchair graphene nanoribbons. The thesis is organized as follows: In the first chapter we introduce different types of sensors and explain extensively solid states gas sensors. Second chapter is devoted to the consideration of synthesis methods and electronic properties of two main allotropes of carbon – carbon nanotubes and graphene nanoribbons.

In the third chapter, by calculation of the local and average densities of states in the tight-binding model, the effects of finite diatomic and triatomic gas molecule adsorption on the electronic properties of a (10,0) single-walled carbon nanotube are studied. The effects of the gas adsorption is introduced into our calculation via two parameter – hopping integral deviation and on-site energy. The hopping integral deviations and on-site energies varied until the obtained results are same as the experimental and also *ab initio* density-functional results. These hopping integral deviations and on-site energies were used for calculation of the effects of finite concentration adsorption on (10,0) SWCNT. Since the gas molecules are adsorbed randomly by the atoms of the (10,0) SWCNT, the Green function in the equation of motion is random and the local behavior is different from the whole system behavior; hence we should calculate configurationally averaged properties. We approach this using the coherent potential approximation formalism to take the average over all possible adsorbed molecule configurations. We find that it is possible to produce a p-type or an n-type semiconductor by finite concentration adsorption of gas molecule.

Investigation of the gas sensing properties of 8-AGNR is the topic of the fourth chapter. Similar to previous chapter, first we find appropriate hopping integral deviations and on-site energies. Then by using these parameters and the coherent potential

approximation formalism, we investigate the effects for finite concentration gas adsorbeed 8-AGNR. We find that the adsorbed gas molecule could produce states inside the semiconducting energy gap of 8-AGNR and alter it into a p-type or an n-type semiconductor. This could be used as gas sensor.

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Chapter 1

Sensors and their applications

1-1 Sensor

A sensor is a device which measures a quantity such as temperature, speed, pressure, and many other types and convert these quantities into electrical form. The difference between a sensor and a transducer is that the sensor converts the measured quantity into electrical form, while the transducer converts a form of energy into another form of energy.

A good sensor has the following properties:

1- It is sensitive to the measured property. The sensitivity level of sensor depends on the effect of changes in measured quantity on sensor's output.

2- Good sensor does not influence the measured property. When we use a sensor to measure a quantity, using of sensor causes that the value of the measured quantity changes. Therefore, the sensor must be designed such that it has the minimum effect on the value of the measured quantity. Common methods to reduce this impact is making the sensor smaller. Technological progress in manufacturing small size electronic parts allows more and more sensors to be manufactured on the microscopic and nanoscopic scales. In addition, the speed and the sensitivity of these sensors are higher than macroscopic sensors.

3- It is insensitive to other properties.

1-2 Types of sensors

The sensors measure and/or detect many quantities such as temperature, pressure, humidity, motion, or the presence of an object (such as gas molecule) and many other types. The sensors, according to the quantities that they measure, are grouped into different types including: pressure sensor, motion sensor, temperature sensor, humidity sensor, gas sensor and many other types. Each type of these sensors has many versions which can be designed to operate within different ranges or may use a different sensing principle.

In the remainder of this section we introduce some of these sensors and in the next sections of this chapter we explain extensively solid state gas sensors and their applications.

1-2-1 Pressure sensor

A pressure sensor usually is used not only to measure the pressure of fluids (gases or liquids) , but also can be used to measure the other variables such as speed, flow, level, depth, and altitude of a fluid.

Main use of pressure sensor (pressure sensing) is useful in weather instrumentation, aircraft, and other machinery that measuring the pressure is necessary for them. The use of the pressure sensor as altitude sensing is useful in weather balloons, aircrafts, and satellites. As mentioned above the other application of pressure sensor was level/depth sensing, where could be employed to measure the depth of submerged body (such as diver), or level of water in a tank.

1-2-2 Motion sensor

Motion sensor is a sensor that is sensitive to presence of a moving object. They usually measure optical and acoustical changes in the field of view and transform them into an electrical signal. There are three types of motion sensors:

1- Passive infrared sensors (PIR) which are sensitive to body heat.

2- Ultrasonic sensors which can detect a moving object by sending out ultrasonic pulses and measuring the reflections from the surface of the object.

3- Microwave sensors which can detect a moving object by sending out microwave pluses and measure the reflections from the surface of the object.

1-2-3 Relative humidity/temperature sensor

A humidity sensor measures relative humidity (the ratio of the moisture in the air to the highest amount of moisture air at that temperature). Two nearby electrical conductors (such as two metal plates) could create an electrical field between them. This fact is used to make the common type of humidity sensor. These sensors are composed of two conductor plates where a non-conductive polymer film is placed between them. The film adsorb the moisture from the air, and this causes changes in the electrical (and therefore in the voltage) between the two plates. By increasing the moisture in the air, the adsorbed moisture and therefore the changes in voltage increased. The changes in voltage could be converted into digital readings to show the amount of moisture in the air.

The humidity/temperature sensors are used in air conditioning systems, home heating, and humidors or wine cellars. The cars, office, industrial, meteorology stations to report and predict weather are the other instruments or places where the humidity sensors could be used in them.

1-2-4 Gas sensor

Gas detection is important in a wide range of activities[1]. For example, gas sensor is used to detect toxic gases in mines or to detect volatile organic compounds generated from food which are important in the food industry. Also gas sensors have extensive applications in homeland security, medicine, and environmental monitoring.

Gas sensor could be used to detect the single gases (O_2, CO, NO, NO_2, etc) and the monitoring of changes in the ambient. Single gas detection is important in controlling of ventilation in cars and planes, detecting fire, detecting a gas leakage, and in alarm devices. Other application of gas sensors is to use them in food industry and in indoor air quality. In this application the gas sensor are used to detect volatile organic compounds or smells generated from food or domestic products. To analyze such complex environmental mixtures, the multi-sensors designed where often referred to as electronic noses[2-4]. Summary of the applications for gas sensor are:

1- Safety

a- Fire detection

b- Leak detection

c- Toxic/flammable/explosive gas detectors

d- Boiler control

e- Personal gas monitor

2- Food

a- Food quality control

b- Process control

c- Packaging quality control (off-odors)

3- Automobiles

a- Car ventilation control

b- Filter control

c- Gasoline vapor detection

c- Alcohol breath tests

4- Environmental control

a- Weather stations

b- Pollution monitoring

5- Indoor air quality

a- Air purifiers

b- Ventilation control

c- Cooking control

6- Industrial production

a- Fermentation control

b- Process control

7- Medicine

a- Breath analysis

b- Disease detection

1-3 Solid state gas sensor

The most applicable type of gas sensors is solid state gas sensors, which also are the best candidates for development of gas sensors. Solid state gas sensors have numerous advantages which cause this great interest in them. Some of these advantages are, small sizes, high sensitivities in detecting very low concentrations, ability in detecting a wide range of gaseous chemical compounds, possibility of on-line operation, and low cost. Solid state gas sensor have different types:

1- Semiconductor gas sensors

2- Field effect gas sensors

3- Piezoelectric sensors

4- Optical sensors

5- Catalytic gas sensors

6- Electrochemical gas sensors

1-3-1 Semiconductor gas sensors

Semiconductor gas sensors are based on metal oxides such as SnO_2, TiO_2, InO_3, etc and known also as chemo-resistive gas sensors.

The gas-sensing mechanisms is based on gas/semiconductor surface interactions such as reduction/oxidation processes, adsorption of the chemical species on the semiconductor or adsorption with surface , chemical reactions between different adsorbed chemical specie, etc. These interactions occur at the grain boundaries of the polycrystalline oxide film. These surface phenomena cause changes in electrical resistance. The change in electrical resistivity could be perceived and used to detect chemical species.

The charge-transfer model and the modified band model could be used to understand the influence of these surface chemical phenomena on the sensor behavior[5]. According to this model, the changes in the electrical resistance of the sensor are described by deformation of depletion space-charge layers at the surface and around the grains, with upwards bending of the energy bands.

The effect of gas/solid state gas sensor interaction may cause changes in the surface conductance or in the bulk conductance of solid state gas sensor. Corresponding to two different changes conductance, two types of gas sensors based on metal oxide could exist[6,7].

The oxygen vacancies are the main bulk defects in the semiconductor oxide. At high operating temperature (600-1000 °C) the oxygen partial pressure change. In such conditions the oxygen vacancies diffuse from the interior of the grain to the surface and vice versa and this causes a change in bulk conductance. The main application of these sensors is to use them in combustion control systems where the measurement of oxygen partial pressure is necessary, in particular in the feedback control of the air/fuel ratio of automobile engine exhaust gases and to reduce the harmful emission of gases such as CO, NO and hydrocarbons [8,9].

As mentioned above, the other type of semiconductors gas sensors is based only on changes in surface conductivity. In this case the change in surface conductivity occurs at low temperature (less than 600 °C) and at quasi-constant oxygen partial pressure. This type of semiconductor gas sensor is known as resistive-type gas sensors.

The semiconductor oxide gas sensor are used extensively. For example, They can be used in electronic [10]. The other important application of is to use them in the food industry.

1-3-2 Optical gas sensors

The optical gas sensors are more useable than the other gas sensors. Features of these sensors including safety, low power consumption, remote sensing, and multiplexing of sensor arrays are advantages of theses sensors over the other sensors such as electrical gas sensors [11].

The optical gas sensors could be used for measuring the chemical and biological quantities. The measurement of changes in absorption spectrum was the first method to detect the desired quantity. But newest optical gas sensors use other methods including epectroscopy, surface Plasmon resonance, and interferometry [12-15].

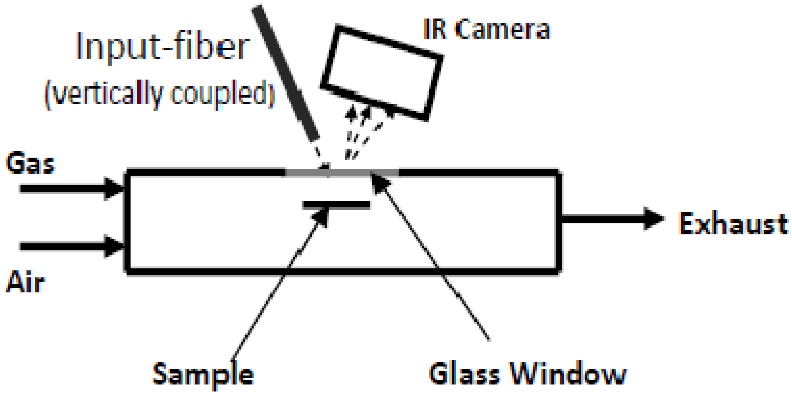

Figure 1-1 Scheme of a optical gas sensor.

1-3-3 Electrochemical gas sensors

Electrochemical gas sensors are based on this fact that chemical reactions at an electronic conductor interface exchange electric charges. Electrochemical gas sensors employ an electrochemical cell. The casing of this electrochemical cell [Fig.1-1] composed of chemical reactants in contact with the surrounding through two terminal (an anode and a cathode) of identical composition and the top of casing has a membrane which can be permeated by the gas sample. Oxidization and reduction takes place at the anode and at the cathode respectively. A current is created as the positive ions flow to the cathode, and the negative ions flow to the anode. Gases such as O_2, and NO, which are electrochemically reducible, are sensed at the cathode while electrochemically oxidizable gases such as CO, NO_2, and H_2S are sensed at the anode [16].

The electrochemical gas sensing is potentiometric or amperometric. This classification depends on whether the output is an electromotive force or an electrical current. Potentiometric measurements are performed under conditions of near-zero current. Amperometric sensors are usually operated by imposing an external cell voltage sufficiently high to maintain a zero oxygen concentration at the cathodic surface; therefore, the sensor current response is diffusion controlled.

Solid state electrochemical devices are the most used sensors type for the measurement of oxygen for automotive market (legislation has restricted the permitted emissions levels of CO, NO_2 and hydrocarbons). Potentiometric sensors based on YSZ (yttrium oxide-stabilized zirconium) together with three-way catalyst system (TWC) represent the most used system for emission control at this time, where the gas sensing operation of the TWC system is based on oxidizing carbon monoxide and unburned hydrocarbons and reduce nitrogen oxides [17].

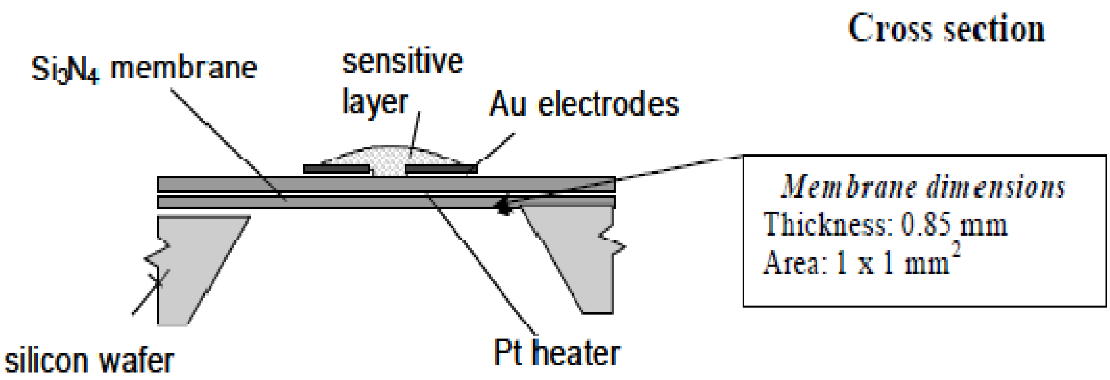

Figure 1-2. Scheme of a closed-membrane type gas sensor. In particular, the model of microhotplates is fabricated at the Institute of Microtechnology (IMT) of Neuchâtel in Switzerland.

Albeit Solid-state chemical sensors have been widely used, but they also suffer from limited measurement accuracy and problems of long-time stability. However, recent advances in nanotechnology, i.e. in the cluster of technologies related to the synthesis of materials with new properties by means of the controlled manipulation of their microstructure on a nanometer scale, produce novel classes of nano-structural materials with enhanced gas sensing properties providing in such a way the opportunity to dramatically increase the performances of solid state gas sensors.

Chapter 2

Carbon nanotubes and graphene nanoribbons

2-1 Carbon and it's allotropes

The carbon atom is one of the first-row elements of the Periodic Table. These elements have atomic orbitals that can hybridize. The reason of this phenomena is the proximity of the energy level of the s-orbital and p-orbitals of carbon's second electronic shell. This property of the carbon atom allows it to form a number of hybridized atomic orbitals with different geometries (sp^1, sp^2, and sp^3) (Figure 2-1). The sp^3 hybridized orbital has a tetrahedral symmetry. The geometry of the sp^2 hybridized orbital is trigonal planar and the sp hybridized orbital has liner symmetry. The type of bonds of carbon atom in the elemental substances is covalent. The properties of covalent bonds depend on the directions of bonds. This in turn gives carbon atom the ability to adapt into various molecular and crystalline structures with different properties. For example, the diamond is non-conductive and has the highest hardness while graphite is conductor and soft.

The allotropes of carbon (Figure 2-2) are:

1) Diamond

2) Graphite

2-1) Graphene

3) Amorphous carbon

4) Buckminster-fullerenenes

  4-1) Buckyballs

  4-2) Carbon nanotubes

  4-3) Carbon nanobuds

5) Glassy carbon

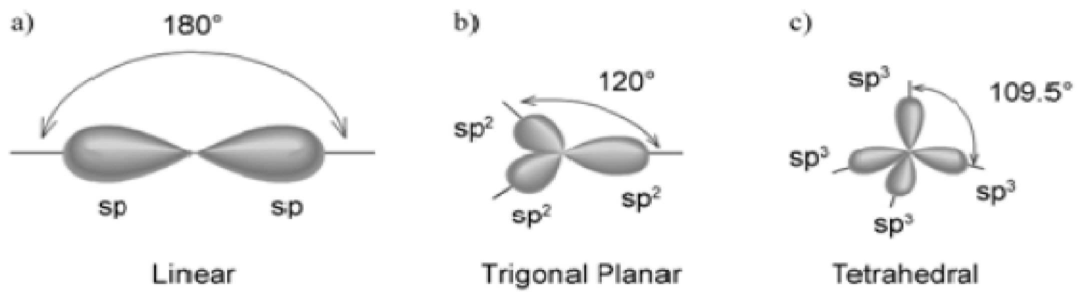

Figure 2-1. The three different hybridisations of carbon a) sp^1, b) sp^2, c) sp^3.

6) Carbon nanofoam

7) Lonsdaleite (hexagonal diamond)

8) Linear Acetylenic Carbon (LAC)

2-1-1 Diamond

Diamond is the singular allotrope of carbon where the type of it's hybrid orbitals is sp^3. So diamond lattice is a variation of the face centered cubic structure (Figure 2-2).

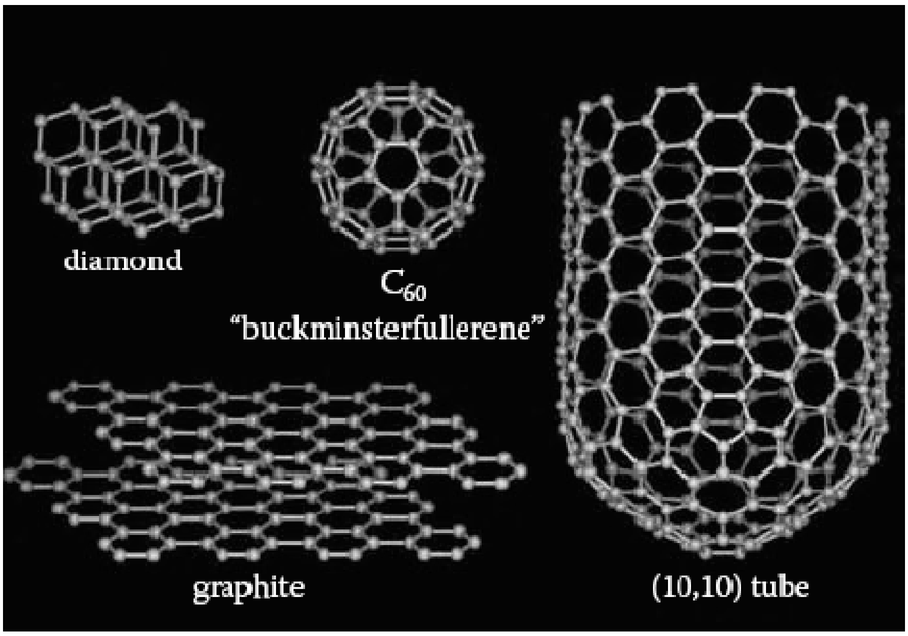

Figure 2-2. Some of the carbon's allotropes.

The special type of hybrid orbitals of diamond donate particular properties to it (most of these properties originate from the strong covalent bonding between its atoms). For example, the hardness and thermal conductivity of diamond is higher than those of all bulk materials (the thermal conductivity of diamond is about five times better than copper). Different factors including its purity, crystalline perfection and orientation can affect the diamond hardness. The hardness of perfect, pure crystals oriented to the (111) direction is higher the it of other crystals (along the longest diagonal of the cubic diamond lattice) [18].

Diamond has very poor electrical conductivity so that most diamonds are excellent electrical insulator[19], but some kinds of diamond (blue diamonds) are natural semiconductors. Boron impurity in blue diamond is origination of their conductivity [19].

2-1-2 Graphite

Graphite is one of the most common allotropes of carbon. In graphite, the s-orbital, p_x and p_y orbitals of carbon hybridize and create three sp^2 hybridized orbitals. Each carbon atom covalently bonded to three other carbon atoms in a plane (hexagonal network). The electrons of these bonded orbitals do not play a key role in its electronic properties. Fourth valance electrons (π bond electrons) of carbon atoms delocalize above and below the planes of carbon atoms and are free to move throughout the plane. These delocalized electrons are responsible for electrical conductivity of graphite along the planes of carbon atoms. But in diamond all four valance electrons of each carbon are covalently bonded and are delocalized. So graphite is conductor while diamond is insulator. The graphite does not does not conduct electricity in a perpendicular direction to planes. The other role of the π bond electrons is that they are origination of a weak van der vaals force that bond planes of graphite.

Graphite is the most stable form of carbon, so it is used in thermo-chemistry as the standard state for defining the heat of formation of carbon compounds. Because graphite conducts electricity, it can be used as material in the electrodes of an electrical arc lamp.