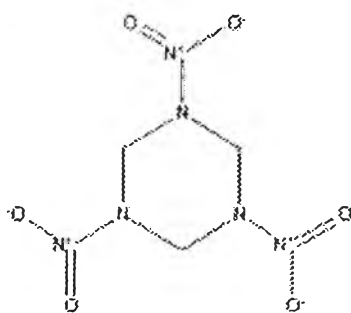


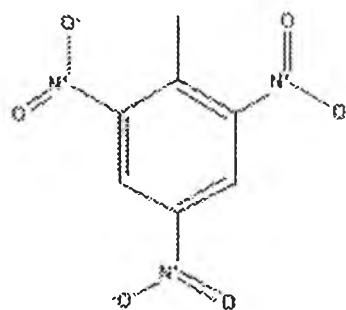


CHAPTER I INTRODUCTION

Semiconductor gas sensors are widely used in both domestic and industrial applications due to their favorable characteristics such as low cost and the increasing demand for energy. The combustion of petroleum products such as diesel oil, heating oil, and heavy fuel oil generates pollutant emissions in the environment. Air pollution is the main environmental problem for all cities. Most toxic gases, for example, carbon monoxide (CO), can cause chest pain in heart patients, headaches, nausea and reduced mental alertness. Sulfur dioxide (SO₂) can induce a lung disease and breathing problems for asthmatics. Emission of sulfur dioxide also leads to the deposition of acid rain and other acidic compounds over long distances -often more than 1,000 kilometers from their source. Such deposition changes the chemical balance of soils which can lead to the leaching of trace minerals and nutrients critical to trees and plants. In addition, bomb explosions in many areas still occur, and we need to develop a way to provide a warning for possible explosions by using gas sensors via the volatiles of bomb chemicals, such as cyclotrimethylenetrinitramine (RDX), trinitrotoluene (TNT), and ammonium nitrate.



TNT



RDX

Figure 1.1 The formulae of trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX).

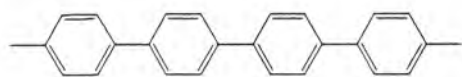
Chemical sensor technologies play an important role in development and improvement of public health and environment (Weetal, 1999). Conducting polymers are unique among the sensing materials known to us at present. They have many advantages over conventional metal sensors; they are lighter and less expensive, they can be operated at lower applied voltage and temperature (Densakulprasert *et al.* 2005) and have a degree of versatility that enables the design and assembly of materials capable of a diverse range of molecular interactions (Barisci *et al.* 1996).

Conducting polymers have some similarities to conventional polymeric materials, but they can be clearly distinguished by the extensive main chain π -conjugation. Conjugated polymers have alternating single- and double- carbon-carbon bonds along the polymer backbone which leaves one unhybridized p-z orbital sticking up out of the plane of the polymer. The electrons in these π -orbitals form a delocalized electron cloud, which is free to conduct electrons. The alternating bond length of the single- and double- carbon-carbon bonds creates an energy gap in the Fermi level, giving rise to a conduction band and a valence band, and thus the semiconducting behavior (Heeger 2002).

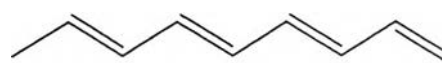
Conducting polymers are widely used in many different types of device: one of them is the chemical sensor. Traditional versions of these have perhaps a dozen electrodes coated with polymer composites, such as polymers mixed with carbon black. Each electrode has a different type of polymer. When these compounds are exposed to a specific gas, this causes in turn a swelling in the polymer and alters the electrical conductivity. The pattern of conductance variations across the dozen polymers provides a signature for that specific gas (Collins 2004).

The possibility of doping conjugated polymers to create a conducting or semiconducting material was discovered in the 1970s by Alan J. Heeger. Organic electronic devices come in two broad classes: small molecules (Fig. 3a) and conjugated polymer chains (Fig. 3b), both of which have alternating double and single carbon bonds. Electrons in double bonds become delocalized. Consequently, the allowed states of the electrons to form bands over ranges of energy (*bottom*). The electrical properties of the material depend on the separation and the filling of the bands. Generally, the polymers have a full valence band, making them insulating. When dopant chemicals (such as sodium) are added, electrons are distributed to the

conduction band or removed from the valence band enable a current to flow (Collins 2004).

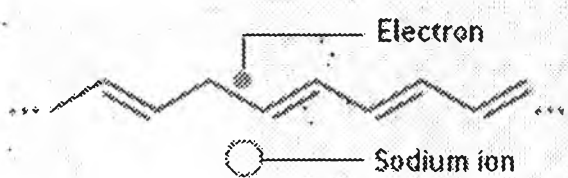


a.) Small molecule

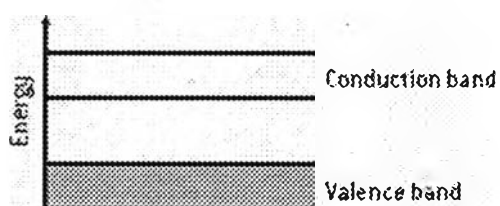


b.) Conjugated double bond

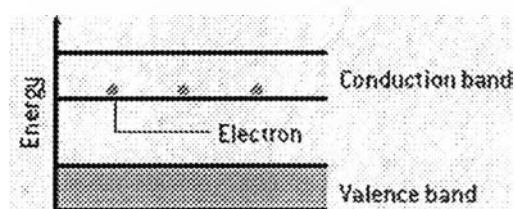
Figure 1.2 The structures of organic conductors: (a) small molecule and (b) conjugated double bond.



a.) doped polymer



b.) band of insulator



c.) band of semiconductor

Figure 1.3 The structures of organic conductors: (a) small molecule and (b) conjugated double bond.

Poly(phenylene vinylene) was the first conductive polymer to obtain a soluble electroluminescent polymer (Yang *et al.* 1992). PPV can be synthesized to obtain a high molecular weight polymer. The first step is the formation of the precursor *via* the Wessling route (Wessling 1972), followed by the synthesis of the polymer from such precursor *via* the thermal reaction (Lenz *et al.* 1988).

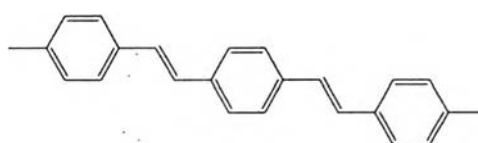


Figure 1.4 Molecular structure of PPV.

PPV has been synthesized to obtain a high molecular weight polymer from a precursor by the Wessling route (R.A. Wessling 1972), and the precursor can form the polymer by the thermal reaction (Lenz *et al.* 1988).

In recent years, zeolites have attracted increasing attention in the field of chemical sensor applications (Yan *et al.* 1999). Composites consisting of zeolites that are dispersed in an organic polymer matrix are widely used in different types of chemical sensors in order to increase their selectivity and to detect toxic gases (Rosa *et al.* 2004).

Zeolites are crystalline, hydrated aluminosilicates of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium, and barium. Structurally the zeolites are “framework” aluminosilicates (fig. 4) which are based on an infinitely extending three-dimensional network of $[\text{AlO}_4]^{5-}$ and $[\text{SiO}_4]^{4-}$ tetrahedral (fig. 5) linked to each other by sharing all of the oxygens (Breck 1973). The framework contains channels and interconnected voids which are occupied by the cations and water molecules. The cations are quite mobile and may be easily exchanged, to various degrees, by other cations.

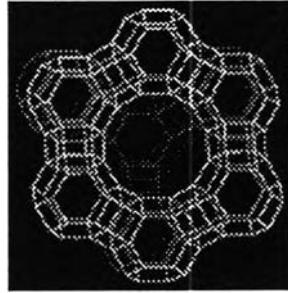


Fig. 1.5 FAU of structure of Zeolite Y.

Zeolites empirical formula is $M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$. The framework contains channels and interconnected voids which are occupied by the cations and water molecules. The cations are quite mobile and may be easily exchanged, to various degrees, by other cations.

Zeolites have pores of a molecular size, which gives rise to strong molecule-pore wall interactions. These interactions are responsible for interesting applications of zeolites when they are prepared as films or membranes. Also, zeolites (mostly LTA and FAU zeolites) have been employed to modify the surface of conventional chemical electrodes in order to increase their electroanalytical performances. Zeolites have attracted increasing attention in the field of chemical sensor applications (Yan *et al.* 1999).

The main problem for semiconductor gas sensors can be related to the interference from other molecules, such as water or organic compounds. This gives rise to a lack of selectivity. Recently, zeolites have been advocated as a means of increasing the selectivity of SnO_2 gas sensors: for example, layers of previously synthesized crystals of zeolites FAU and FER were coated on to cover the sensing layer in order to increase selectivity and sensitivity of gas sensor (Fukui *et al.* 1997).