

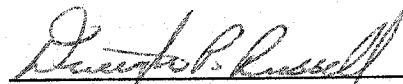
PREVIEW

NO₂ SENSING WITH BISMUTH MOLYBDATE THIN FILMS

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Department of Physics

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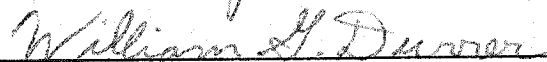
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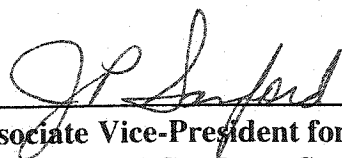
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**Associate Vice-President for
Research and Graduate Studies**

Dedicated to my Parents:

Elpidio Luna and Gabriela Agustin,

To my wife Lilliana and in memoir

of my best friend:

Gilberto Trinidad Martínez Pérez

PREVIEW

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NO₂ SENSING WITH BISMUTH MOLYBDATE THIN FILMS

by

NICOLAS LUNA, B. S.

THESIS

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PREVIEW

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ABSTRACT

Bismuth Molybdate thin films are experimentally tested as gas sensors. Chemical synthesis of Bismuth Molybdate catalyst was the first step to get the films. The method used to synthesize the catalyst was the co-precipitation. The films are elaborated from this catalyst powder, by thermal evaporation in vacuum. Identification of the crystallographic phase obtained after chemical synthesis was determined by the use of the X-Ray diffraction technique. After identification, the thermal evaporation was performed. At the first stage, the films showed an amorphous phase_[17], consequently a thermal treatment to recover their crystallinity was determined and performed. A chamber of pyrex glass was specially designed and constructed to make the electrical characterization of the films in presence of NO₂. The results obtained from this procedure show that Bismuth Molybdate detects the gas at low concentrations and at low temperatures. The development of an additional experiment showed that we have a reversible reaction of the gas and the film at low temperatures and that the theory of the exchange of lattice oxygen for this catalyst is still valid.

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INTRODUCTION

Bismuth Molybdate and other mixed Metal Oxide catalysts are frequently employed to effect the partial oxidation or ammoxidation of light hydrocarbons to produce such important chemical intermediates as Acrolein, Acrylonitrile, Methacrolein and Butadiene. But, in spite of this "classic" role which Bismuth Molybdate plays in studies of heterogeneous catalytic partial oxidation reactions, a new field of application for this material other than catalysis could be developed.

According to studies made on this catalyst, remotion and deposition of lattice oxygen in a reversible manner occurs on its bulk; this property, in principle, could be used to detect specific chemical species. This means that Bismuth Molybdate could be used as a Chemical Gas Sensor.

With this idea, only one attempt to apply such a catalyst as a chemical gas sensor has been done_[1]. Unfortunately, the results obtained are not completely satisfactory. Despite these results, the goal of using Bismuth Molybdate catalytic properties for detection of specific gaseous molecules remains interesting for research.

A new attempt to use Bismuth Molybdate as a gas sensor is developed in this work. To reach this goal, Bismuth Molybdate thin films were prepared. Thin Films were obtained by vacuum evaporation of chemically synthetized powders. A brief X-Ray study was made to identify the crystalline structure of these powders and compare them with the most accepted crystalline structure reported. Microscope slides were used as substrates. The electronic characterization of films within gaseous atmospheres (small amounts of NO₂ in Nitrogen) was developed in a special glass chamber constructed for this task.

Results obtained in this work show that Bismuth Molybdate thin films have a behavior completely different from those reported_[1]. The response to NO₂ is not reported in former papers. This behavior may be due to several reasons given in the work. On this basis, it is claimed that mechanisms involving adsorption-desorption of lattice oxygen in this catalyst,

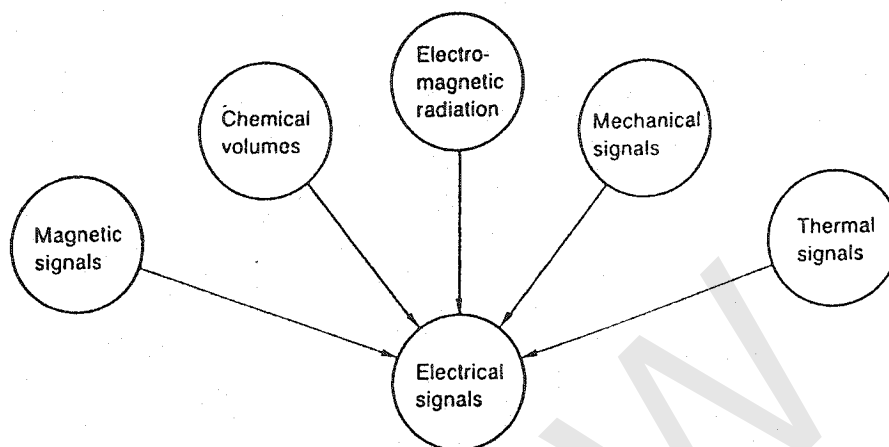


Figure 1.-Physical dimensions which are transformed to electrical signals by sensors.

is still one of the best explanations and that it is important to develop it as much as possible toward manufacturing a reliable Chemical Gas Sensor.

A chemical gas sensor as mentioned above, can be defined as a device which records the concentration of specific particles (atoms, molecules or ions in gases or liquids) using an electrical signal. In the same sense a sensor can be defined as a device which converts (changes in) the physical dimension which is to be measured into (changes in) an electrical dimension which can be processed or transmitted electronically.

The physical dimensions can be classified in accordance with the diagram shown in figure 1_[2]. In order to compare different types of measurands and sensors, a flexible classification scheme has been proposed_[3]. Table 1 list the measurands which are defined as the input quantities, properties or conditions that are detected or measured by sensors. We can see that chemical signals are very different from physical signals and that chemical and physical sensors also differ greatly. This is true because approximately 100 physical measurands can be recorded using physical sensors, but for chemical sensors, this number is larger by several orders of magnitude (the same as elements and chemical compounds we can find). It is in this fact where the importance of chemical sensors is based.

Detection of specific particles as defined above is in many cases no real problem since

TABLE 1 Measurands

1. Acoustic
1.1 Wave amplitude, phase, polarization, spectrum
1.2 Wave velocity
1.3 Other (specify)
2. Biological
2.1 Biomass (identities, concentrations, states)
2.2 Other (specify)
3. Chemical
3.1 Components (identities, concentrations, states)
3.2 Other (specify)
4. Electric
4.1 Charge, current
4.2 Potential, potential difference
4.3 Electric field (amplitude, phase, polarization, spectrum)
4.4 Conductivity
4.5 Permittivity
4.6 Other (specify)
5. Magnetic
5.1 Magnetic field (amplitude, phase, polarization, spectrum)
5.2 Magnetic flux
5.3 Permeability
5.4 Other (specify)
6. Mechanical
6.1 Position (linear, angular)
6.2 Velocity
6.3 Acceleration
6.4 Force
6.5 Stress, pressure
6.6 Strain
6.7 Mass, density
6.8 Moment, torque
6.9 Speed of flow, rate of mass transport
6.10 Shape, roughness, orientation
6.11 Stiffness, compliance
6.12 Viscosity
6.13 Crystallinity, structural integrity
6.14 Other (specify)
7. Optical
7.1 Wave amplitude, phase, polarization, spectrum
7.2 Wave velocity
7.3 Other (specify)
8. Radiation
8.1 Type
8.2 Energy
8.3 Intensity
8.4 Other (specify)
9. Thermal
9.1 Temperature
9.2 Flux
9.3 Specific heat
9.4 Thermal conductivity
9.5 Other (specify)
10. Other (specify)

it is a task that can be performed by using Analytical Chemistry techniques such as Gas Chromatography, Mass Spectrometry, etc. But, because of the requirements of expensive equipment and discontinuous function, the use of chemical sensors with properties such as small, robust and reliable construction, microelectronics compatibility, reproducibility, selective and rapid response, greatest possible independence from environmental parameters and manufacturability using conventional microelectronics methods, have a growing

demand. These requirements mean that there is an extensive range of applications. Some of these examples are found in measurements of emissions and environmental protection, measurements of fire prevention and explosions, process measurements (for example in chemistry, food industry, biotechnology, etc), medicine, automobile technology, household equipment, water preparation, sewage analysis, surface and materials analysis, etc.

As mentioned above, detection of specific particles using chemical semiconductors sensors is the ideal of researchers in this field. They want to accommodate a complete integrated analytical chemistry laboratory on a single chip. However, in reality this is still a very remote prospect. Another factor of this interest in chemical gas sensors is the increasing complexity of many processing procedures, as well as the desire to economize in the use of energy and raw materials and to reduce environmental pollution.

With this aim, Bismuth Molybdate Thin Films do not solve the problems mentioned above, but increase the number of prospective thin film materials that could be analyzed and studied to integrate a gas sensor device.

CHAPTER 1

THEORETICAL BACKGROUND_[7]

INTRODUCTION

A simple sensor for the detection of specific molecules from a molecular mixture is schematically represented in figure 2. In this example the linear triatomic molecule of CO_2 forms an adsorption complex with the surface atoms of the sensor. This complex can either accept electrons from or donate them to the conduction band of the sensor. The properties of the molecule which allow it to be an acceptor or donor at the surface cause the concentration of free carriers in the semiconductor to decrease or increase. This brings about a corresponding change in conductivity which makes the electronic detection of the particle possible.

This is the most acceptable theory to describe the mechanisms of adsorption-desorption on metal- oxide semiconductors. This theory has its background in the explanation by Brattain and Bardeen of 1952 and published in 1953_[4]. In this, they showed experimentally and theoretically the process of adsorption and desorption on cleaned surfaces of Germanium using the contact potential method. From this theory up to now, some modifications have been made to fit them to the new materials under study.

The use of metal-oxide sensors with thin film technology was presented in 1962. ZnO thin films_[5], were prepared by vacuum evaporation and subsequent oxidation in air; they showed changes in conductivity when exposed to different gases. After this, SnO_2 became the first material used for commercial sensors which are known now as "Taguchi Gas Sensors"_[6] due to the developer of this sensor. This type of sensor has several problems, but for many applications these problems are well compensated by the low cost of the sensor and by its sensitivity in detection of combustible gases (such as Hydrogen and Hydrocarbons in

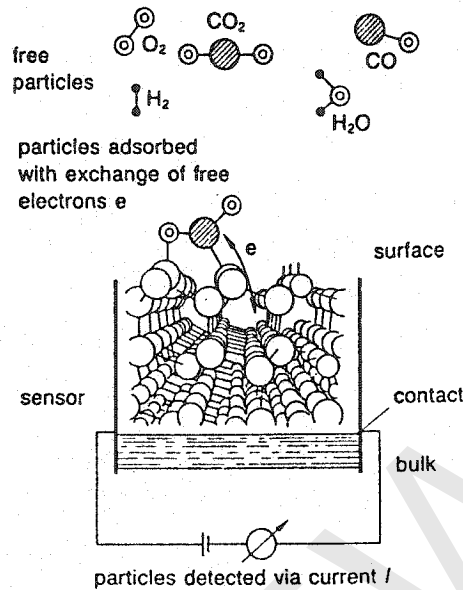
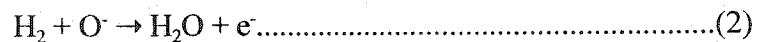
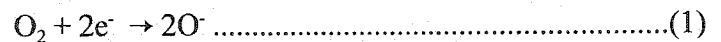


Figure 2.-Model of the surface of a chemical gas sensor.

air). The operation of Metal-Oxide sensors, as mentioned above, is based in the decrease of resistance of a layer of powdered SnO_2 if a combustible gas is present in the ambient atmosphere.

The change of resistance in a metal-oxide semiconductor is due to the fact that, in air, oxygen adsorbs on the surface, dissociates to form O^- , where the electron is extracted from the semiconductor. This electron extraction tends to increase the resistance (assuming an n -type semiconductor). In the presence of a combustible gas, say Hydrogen, the hydrogen reacts with the adsorbed O^- to form water and the electron is re-injected into the semiconductor, tending to decrease the resistance. A competition results between oxygen removing electrons and the combustible gas restoring these electrons. So then, the steady-state value of the resistance depends on the concentration of the combustible gas. To illustrate this we could have the competing reactions:



and so the more H_2 present the lower of density of O^- , the higher the electron density in the semiconductor and thus the lower the resistance.

A second model which exists or coexists is that the combustible gas, if chemically active,

extracts a lattice oxygen from the metal oxide, leaving vacancies that acts as donors. The oxygen from the air tends to re-oxidize the metal-oxide, removing the donor vacancies. Thus there is a competition between the oxygen removing donor vacancies and the combustible gas producing donor vacancies. The density of donor vacancies (and hence the resistance) then depends only on the concentration of combustible gas because the oxygen pressure is constant (as when operating in air).

A catalyst is usually provided to accelerate the reaction rate; then it is expected that the response of the sensor could be rapid and selective. A sensor made of catalytic materials or with a catalyst added could improve the characteristics of such a sensor; in this sense catalysis plays an important role for the detection of gases.

From above paragraphs, it is clear that to understand the operation of chemical sensors based on metal-oxide semiconductors, we must examine in more detail how adsorbed gases affect the semiconductor resistance, how the extraction of lattice oxygen affects the semiconductor resistance, how the combustible gases interact with the adsorbed oxygen or with the lattice, how catalysts improve the combustible gas/oxygen reaction, how a catalyst itself can be used as a gas sensor and finally how all these chemical and physical processes can be controlled to yield a useful gas sensor. It is recognized that, because this is a relatively new field, much of the information obtained up to now has only experimental background. We have a well established and known theory of semiconductor materials, but for the metal-oxide materials used for gas sensors we have some theories which combine semiconductor, catalysis, chemical and surface theories.

1.1.-SEMICONDUCTORS

1.1.1.-THE BULK

1.1.1.a.-Band Model

Electrons in a crystalline material are only allowed to have energies within certain ranges

or bands. Bands of energy levels, rather than discrete levels, form because electron interaction separates the levels, as described by the Pauli principle. Between bands, energy levels are quantum mechanically disallowed, and those regions of energy are termed *band gaps*.

In a semiconductor the highest energy band completely filled with electrons is called the *valence band*. At zero temperature, the valence electrons in a semiconductor occupy all the available energy levels within the valence band. Normally there are an integral number of energy levels in each band, one for each valence electron from each atom in the solid. (Because the valence band typically will span an energy range larger than the number of electrons available, then, the individual energy levels in the band are not resolvable). For this reason, it is customary to use the term *density of states* to mean the number of energy levels per unit energy at a given energy, that is, $\Delta n / \Delta E$.

The next excited state above the valence band into which the electrons can be excited is called the *conduction band*. In a perfect semiconductor at 0 °K the conduction band is empty of electrons. Of course, any real solid can be naturally or artificially imperfect, leading often to some electrons in the conduction band or some missing electrons (i.e. *holes*) in the valence band. Figure 3 illustrates the "classic" band model of the ideal semiconductor.

1.1.1.b.-Fermi Function

Under thermal equilibrium conditions, the distribution of electrons over different energy levels is given by the Fermi Function f :

$$f = \left\{ 1 + \exp \frac{[E - E_F]}{kT} \right\}^{-1} \dots\dots\dots(3)$$

where k is the Boltzmann constant and T is the absolute temperature. This function gives the probability that a level with energy E will be occupied with an electron. The Fermi energy E_F is the energy for which f is $\frac{1}{2}$ such that an allowed level at that energy has an equal

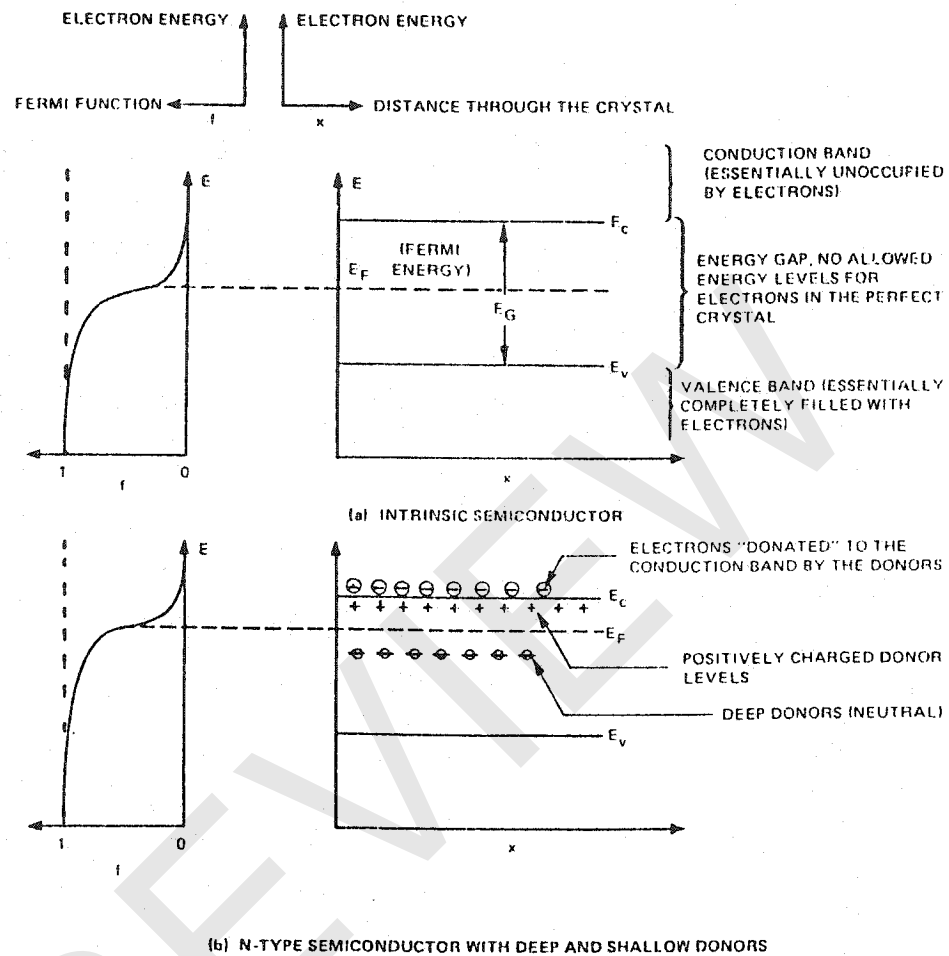


Figure 3.-Band diagram for "classical" semiconductors and Fermi level localization.

chance of being found occupied or empty. Derivation of equation 3 does not depend on the type of band structure in the solid. The occupancy of the energy levels in a solid can be determined for any material by superimposing the Fermi function over the band structure while requiring overall electrical neutrality. The Fermi function is shown graphically in fig. 3. For an energy level at $E \ll E_F$ the function approaches 1, thus such an energy level E is almost certainly occupied. For the semiconductor in fig. 3(a) with no energy levels in the band gap, the Fermi level is situated very near to the middle of the band gap, since the number of electrons in the conduction band is equal to the number of holes in the valence