DEVELOPMENT OF SENSORS BASED ON ADVANCED MICRO- AND NANO- STRUCTURED CARBON MATERIALS

By

Frank Willi Mendoza Centeno

A thesis submitted in the partial fulfillment of the requirement for the degree of

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DEVELOPMENT OF SENSORS BASED ON ADVANCED MICRO- AND NANO-STRUCTURED CARBON MATERIALS

Accepted by the Faculty of the Doctoral Program in Chemical Physics of the University of Puerto Rico in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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May 2014
To Opus Dei

...Lord, I can’t stay away...
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ABSTRACT

The thesis is focused on the development of sensors based on advanced micro- and nano-structured carbon materials. In particular, we developed prototype diamond-based ultraviolet photodetectors and carbon nanotubes-based gas sensors. We describe the method of preparation and characterization of the active carbon-based materials and their structural and compositional characterizations. This is followed by the corresponding device fabrication and testing.

The first part of the thesis briefly gives an introduction to our current understanding about carbon materials, with emphasis on synthetic diamond and bamboo-like carbon nanotubes, and to the materials’ properties that are useful for ultraviolet photodetectors and gas sensor applications. The rest of the thesis is organized as follows:

In the Chapter 2, the room-temperature photosensitivity of sulfur-assisted micro- (MCD), submicro- (SMCD) and nano- (NCD) crystalline diamond films synthesized by hot-filament chemical vapor deposition was studied. The structure and composition of these diamond materials were characterized by Raman spectroscopy, scanning electron microscopy and X-ray diffraction. The UV sensitivity and response time was studied for the three types of diamond materials using a steady state broad UV excitation source and two pulsed UV laser radiations. It was found that they have high sensitivity in the UV region, as high as $10^9 \text{sec}^{-1} \text{mV}^{-1}$ range, linear response in a broad spectral range below 320 nm, photocurrents around $\sim 10^{-5}$ A, and short response time better than 100 ns, which is independent of fluency intensity. A phenomenological model was applied to help understand the role of defects and dopant concentration on the materials’ photosensitivity.
Chapter 3 expands on the usefulness of polycrystalline and nanocrystalline diamond films for UV sensor applications by exploring the field emission device configuration and the grain-size effect on the photo-response. Different grain sizes of crystalline diamond were grown to assess the changes to the photo-response behavior in the 200 to 300 nm wavelength range covering the band gap energy (5.5 eV or 225 nm). The comparison of the photo-response in the samples was evaluated by means of two types of contact electrode configurations. The first configuration operates in the well-known planar configuration (PC) with electrodes on S-assisted diamond surfaces while the second operates in an electron field emission (FE) mode at low electric field (0.7V/µm - 1.7V/µm) such that only ultraviolet light can trigger the emission current. Compared with samples in a planar configuration, the field emission performance of S-assisted diamond films can be greatly enhanced by the UV light illumination. Additionally, samples of interest measured in FE mode confirmed information about the grain boundary and negative electron affinity (NEA, $\chi$) which are believed are the responsible for the electrical response observed in samples.

Chapter 4 describes chemical sensors based on tin dioxide-carbon nanotubes (SnO$_2$-CNT) composite films that were fabricated by hot filament chemical vapor deposition (HF-CVD) technique. The composite films consist of SnO$_2$ nanoparticles highly dispersed on the CNTs surface. Their resistivity is highly sensitive to the presence of adsorbates, which become easily attached or detached at room temperature and ambient pressure depending on their gas phase concentration. We systematically studied the sensitivity of the SnO$_2$-CNT composite films for ethanol, methanol and H$_2$S. The results were also compared to those for SnO$_2$ and CNTs separately. It is shown that the
SnO$_2$-CNT composite films can detect ethanol, methanol and H$_2$S down to ppm levels below OSHA’s permissible exposure limits at room temperature and ambient pressure. Moreover, they self-recover within one minute without requiring any heating or energy source.

Chapter 5 describes another oxide-based material integration with carbon nanotubes under a new method. We developed to synthesize nano-size barium strontium titanate Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST) maize bead-like structures conformally coated on Bamboo-like carbon nano-fibers (BCNTs). Initially BCNTs were fabricated by hot-filament chemical vapor deposition (HF-CVD) techniques on Cu substrates. Later, BST was deposited on BCNT/Cu by pulsed laser deposition (PLD) techniques. Surface morphology, cross-sectional image and topography of the BCNTs and BCNT-BST maize-like nanostructures were investigated by X-ray, field-emission scanning electron microscopy (FE-SEM), Raman spectroscopy and tunneling electron microscopy (TEM) techniques. BST-BCNT hybrid structures provide an additional degree of freedom to interconnect the oxides, which in turn provides [3D] geometry for functionality. There had been a popular misconception that oxides cannot grow on CNT at high temperature; this long-standing problem has now been solved. The present unregistered nanostructures can be used as sensors; however, if these structures are made as registered arrays, they can be used as nonvolatile memory elements and high energy density capacitors.

Finally, on Chapter 6, we give an overview of the experience gained through this research, and some suggestions for those who would like follow the research methods employ here. It provides experimental information learned through experience that may be helpful and avoid delays to the newer experimentalists.
THESIS RELATED PUBLICATIONS

PEER-REVIEWED PUBLICATIONS


ORAL PRESENTATIONS


4. “UV Photosensitivity of the Polycrystalline CVD Diamond”, International Symposium on integrated Functionalities (ISIF-2010), San Juan, Puerto Rico, June 13-16, 2010

POSTER PRESENTATIONS


2. “Room temperature gas sensor of SnO2 - CNT nanocomposite” 33th Puerto Rico Interdisciplinary Scientific Meeting (PRISM), University of Turabo, Gurabo, Puerto Rico, USA, March 9, 2013

3. “Room temperature gas sensor of SnO2 - CNT nanocomposite ”, Group of Physics, University of Puerto Rico, Rio Piedras Campus, College of Natural Sciences, UPR-RP, Lobby of Natural Sciences, San Juan, Puerto Rico, USA, October 18, 2013

4. “Carbon nanofibers as templates of ferroelectric material”, Conferencia Internacional de Materiales (CIM 2011), Bogota – Colombia, noviembre 26-30, 2011


7. “Study of carbon nanostructures by FePc-assisted chemical vapor deposition”, 2010 MRS Fall Meeting. Hynes Convention Center & Sheraton Boston Hotel, Boston, MA, November 29- December 3, 2010

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<th>Meaning</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>B-CNT</td>
<td>Bamboo-like carbon nanotubes</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersion Spectroscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-Ray Analysis</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>FCC</td>
<td>Faced-centered cubic</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>FE</td>
<td>Field Emission</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>g/cm³</td>
<td>gram/centimeter cubic</td>
</tr>
<tr>
<td>GPa</td>
<td>Giga Pascal</td>
</tr>
<tr>
<td>h</td>
<td>Planck constant</td>
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<tr>
<td>HFCVD</td>
<td>Hot-Filament Chemical Vapor Deposition</td>
</tr>
<tr>
<td>HOD</td>
<td>Highly Oriented Diamond</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Ordered Pyrolytic Graphite</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>HRSEM</td>
<td>High Resolution Scanning Electron Microscopy</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>keV</td>
<td>kilo-electronvolt</td>
</tr>
<tr>
<td>Kg/mm²</td>
<td>kilograms/millimeters squared</td>
</tr>
<tr>
<td>MCD</td>
<td>Microcrystalline Diamond</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>mJ</td>
<td>milli-Jouls</td>
</tr>
<tr>
<td>mm</td>
<td>millimeter</td>
</tr>
<tr>
<td>m²/g</td>
<td>meters squared / grams</td>
</tr>
<tr>
<td>MO</td>
<td>Metal-oxides</td>
</tr>
<tr>
<td>η</td>
<td>External Quantum Efficiency</td>
</tr>
<tr>
<td>NCD</td>
<td>Nanocrystalline Diamond</td>
</tr>
<tr>
<td>NEA</td>
<td>Negative Electron Affinity</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>NTs</td>
<td>Nanotubes</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>Ω·m</td>
<td>Ohms per meter</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma Enhanced Chemical Vapor Deposition</td>
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<tr>
<td>RMS</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>S</td>
<td>Sulfur</td>
</tr>
<tr>
<td>S cm⁻¹</td>
<td>Siemens / centimeter</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>------------------------------------</td>
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<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SMCD</td>
<td>Sub microcrystalline diamond</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless Steel</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TPA</td>
<td>trans-polyacetylene</td>
</tr>
<tr>
<td>µm</td>
<td>micro-meter</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>volts</td>
</tr>
<tr>
<td>W/cm K</td>
<td>Watt/centimeter Kelvin</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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The success of this thesis is a tremendous result of help from amazing people. I would like to thank to my advisor Dr. Gerardo Morell for allowing me to be part of their Laboratory, who encouraged me with their help and guidance through graduate school.

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To my family, my pretty Neida and Children, and to my parents Patricia Centeno, Francisco Antonio Mendoza for giving me the tools needed to be successful.
Chapter 1: Introduction

After fulfilling important commitments to the synthesis and characterization on carbon-based materials the next step to this research obey to the need in develop applications with those structures denoted as nanomaterials (materials with 1 to 100 nm of size). The main reason is due to carbon-based materials possess attractive features such as thermal, mechanical or electronic properties and their high surface area to volume ratio, carbon nanomaterials can interact at organic molecules levels under different mechanism. These interactions such as hydrogen bonding, electrostatic forces, van der Waals forces and hydrophobic interaction promotes nanosized structures with a wide range of applications. Specifically, the present report is focused in carbon nanotubes–based gas sensor and diamond-based photodetectors.

1.1. Carbon-based nanomaterials

“Carbon has been investigated for more than half a century without exhausting its wonders and challenges.” — M.S. Dresselhaus.

A variety of carbon allotropes and their different chemical structures associated with their physical properties are largely due to the flexibility of carbon’s valence electrons (hybridization). This effect creates dimensionality of its bonding structures (polymorphism) [1]. In other words carbon can come in many forms or structures.
Figure 1.1 shows a general representation of known structural forms of carbon. Some of them are diamond which is carbons in a tetrahedral lattice arrangement. Graphite with carbons organized in sheets of hexagonal lattice, graphene (single layer of graphite), carbon nanotube (a graphene layer rolled), and buckminsterfullerene (the 60 atom carbon atoms forming a sphere) \[2\]. Graphene is the young material in comparison with diamond and graphite the ancient materials. Graphite can be found as HOPG (Highly Ordered Pyrolytic Graphite), fibers, among others \[3\]. Meanwhile the fullerenes have a variety of molecules composed entirely by carbon. \(C_{20}\) is the smallest, \(C_{60}\) is the most common but also \(C_{70}\), \(C_{72}\), \(C_{80}\) and \(C_{82}\) are also produced by the nature. In the Table 1.1 are visible values mostly representatives and comparatives known about of structures of carbon. Diamond is insulator material while graphene conducts both heat and electricity better than copper. Experimentally, the elastic properties and intrinsic strength of graphene was measured using an atomic force microscope with a diamond tip because conventional silicon tip break before that graphene \[4\]. However, normally graphene is visualized as hundred times stronger than steel \[5\].
Table 1.1. General values of known carbon materials

<table>
<thead>
<tr>
<th></th>
<th>Diamond</th>
<th>Graphite</th>
<th>C_{60}</th>
<th>CNT</th>
<th>Graphene</th>
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<tr>
<td><strong>Color</strong></td>
<td>Colorless</td>
<td>Steel black to grey</td>
<td>Black solid/ Magenta</td>
<td>black</td>
<td>colorless</td>
</tr>
<tr>
<td><strong>Density (g/cm$^3$)</strong></td>
<td>3.515</td>
<td>1.9-2.3</td>
<td>1.69</td>
<td>1.33-1.4</td>
<td>1.5-2</td>
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<td><strong>Specific Gravity</strong></td>
<td>3.52</td>
<td>2.2</td>
<td>1.7-1.9</td>
<td>2</td>
<td>2.2</td>
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<td><strong>Hardness (Mohs Scale)</strong></td>
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<td>1-2</td>
<td>1-2</td>
<td>1-2</td>
<td>&gt;10?</td>
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<td><strong>Melting Point (°C)</strong></td>
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<td>3652-3697</td>
<td>800</td>
<td>graphite</td>
<td>3627</td>
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<td>4200</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
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<td><strong>Electrical Conductivity</strong></td>
<td>Insulator</td>
<td>Conductor</td>
<td>Semiconductor</td>
<td>Conductor to semiconductor</td>
<td>Conductor</td>
</tr>
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<td><strong>Hybridization</strong></td>
<td>sp$^3$-tetrahedral</td>
<td>sp$^2$-trigonal planar</td>
<td>sp$^2$-trigonal planar</td>
<td>sp$^2$-trigonal planar</td>
<td>sp$^2$-trigonal planar</td>
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<td><strong>Crystal Shape</strong></td>
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<td>Tabular</td>
<td>Truncated icosahedron</td>
<td>Cylindrical</td>
<td>2D-plane</td>
</tr>
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</table>

See the references that refer to the websites where found the general information in this table. [6]

1.1.1. Carbon hybridization

Hybridization occurs when the atomics orbitals combine with hybrid orbitals and owing to this, Carbon possesses the property to exist in different forms as four single bounds, carbon of double bonds and two single bonds and as well as carbon of triple bonds and the single bond. This are generally named sp$^3$, sp$^2$ and sp respectively. Carbon have four valence electrons and when talk about sp$^3$ hybridization is due to the three p-orbitals combine the valence electrons whit one s-orbital, forming four equivalent hybrid orbitals. If only one p-orbital does not combine with s-orbital, carbon now forms three hybrids as
s- one and two p-orbitals (sp\(^2\)). The third one sp hybrid basically just one p-orbital combine with s-orbital leaving the other two p-orbitals randomly available to form the triple bonding whit others carbon atoms.

### 1.1.2. Synthetic Diamond

Natural diamond brings together desirable properties that make it one of the most interesting materials under consideration for applications in many areas. The interest in this work was related to optical detectors systems applications to heavy duties. Owing to its wide band gap, diamond can adopt either semiconducting (the blue diamond, type IIb diamond) or insulating (10\(^{11}\) Ω·m) properties. This material is known as hardest (10000Kg/mm\(^2\)) and stiffest than other materials [7]. Diamond shows the highest thermal conductivity (22 W/cm K) in comparison with copper, at list 5 times more. Also diamond show high wear resistant and has tentatively a fracture strength estimated in > 60 GPa [8]. Unfortunately, owing to their high cost, the applications are limited. However to date scientists already have methods to synthesize diamonds. Hence, the progress in diamond growth was introduced since 1980 by Spitsyn et al. [9] using the chemical vapor depositions (CVD) method, off course relatively inexpensive method. In general CVD means deposition of a solid on a heated surface from a chemical reaction in the vapor phase.

After that, many CVD techniques (evaporation, sputtering, molecular beam epitaxy and ion plating among others), around the hydrocarbon gas mixture concept, make possible the diamond fabrication. The CVD methods allow incorporate other elements during the growing diamond process making suitable choice for specific properties in CVD-
diamond according the application required (i.e. input boron source during the CVD process to obtain p-type diamond semiconductor, reliable to transistors).

In this work, the synthesis the materials, was emphasized in hot filament CVD (HFCVD) technique which was introduced since 1979 with high deposition rates as a main feature among others [10]. HFCVD has many advantages compared with other methods, including being much simpler and easier to adopt for large-area deposition at a lower cost, which is special interest for several applications [11], industry purposes. In the fabrication of carbon materials (i.e. diamond, CNT or graphene) using a basic hot-filament CVD system, a gas mixture consisting of a hydrocarbon in hydrogen is decomposed utilizing a refractory metal filament (such as tungsten, tantalum or rhenium), heated and maintained at 2000°C. High filament temperature is very necessary and plays an essential role in creating the gas-phase species that enable and influence carbon material growth. For example, filaments temperatures lower than or equal to 1800°C, little amount or no diamond film was observed. A high filament temperature of over 2300°C was used in order to increase the growth rate. However, under high filament temperatures, filaments are carburized (tungsten case) and become very brittle, resulting in a relatively short lifetime and in changing growth conditions.

1.1.3. Carbon nanotubes

Carbon nanotubes (CNT) are the mostly representative nanomaterial since their discovery in 1991 by Lijima and Ichihashi [12]. Owing to excellent chemical and physical properties CNT are promising their applications in any aspect of nanotechnology [13]. CNT with a high aspect ratio, large specific surface area (Single-Wall > 1600 m² /g,
Multi-Wall > 430 m²/g), with good mechanical and electrical (5000 S cm⁻¹) properties, are widely used as the active material in different fields (scanning probes, batteries, field emitters, sensors and supercapacitors). The synthesis of CNT can be through different techniques, such as electric arc-discharge, laser ablation or chemical vapor deposition. CVD is a common method used for the commercial production of CNT, arc-discharge results in lowest yield and laser ablation is expensive. Forward is explained (chapters 4 and 5), as a special case in this thesis, the advantage to use CNT fabricated under the hot filament chemical vapor deposition (HFCVD) technique. During various efforts to synthesize the materials based on carbon, different manners to grow carbon nanotubes were studied (as a part of the holistic learning of the author). One of them consists in the growth of CNT with the bamboo-like structure, as the most common form [14], directly deposited on copper, as a substrate, using the HFCVD technique [15]. The general result after the deposition can be seen through images from scanning electron microscopy (SEM) and the transmission electron microscopy (TEM). Figure 1.2-a) shows the bamboo-like carbon nanotubes randomly oriented in the form of a porous mat. The figure 1.2-b) shows submicron particles (Cu-spheres) that appear after the deposition process as a part of the product of catalytic behavior of copper (some Cu-spheres seems come from tip growth). While Figure 1.2-c shows that the structure consists of long hollow cavities and periodic empty compartments in the tube with diameters in ranging 50-100 nm at variable lengths. Traces of the amorphous carbon coated the tubes. The especial feature of these carbon nanotubes, among others, consists in that during the growth process no catalyst materials (i.e. most commonly transition metals such as Ni, Co or Fe) were conventionally used.
1.2. Ultraviolet Photodetector

A photodetector is formed by materials (semiconductors - III-V materials) capable of transducing optical energy that absorbs and converts it to electrical energy, which usually manifests as a photocurrent. The general performances required in optical detectors are high sensitivity, low dark current, wide bandwidth, high reliability and low cost. The photodetector concept is widely used in optical telecommunication systems.

Photon detectors are recognized in two groups, photoelectric and photographic detectors [16]. Photographic detectors (currently as active pixel sensor [17]) can record large amount of data in a single photon exposure. Photoelectric detectors are a class of material that obeys at changes the electron flux through its electrodes on incident wavelength dependence. The photographic detector sensitivity is lower in consideration to the photoelectric detector due to drawbacks in the resolution. Photoelectric detectors possess

Figure 1.2. SEM images of, a) show the bamboo-like character obtained with HFCVD. b) Cu catalyst particle and c) high resolution image of TEM of the nano-cavities.

Adapted from Journal of Nanomaterials, Volume 2008, 515890
more sensitivity, stability of response and linearity characteristics. Normally this class of
detectors can develop in form: photoconductive (photodiodes), photovoltaic (solar cell
and photodiodes) and photo emissive (phototubes and photomultipliers). Inside the Table
1.2, it can be seen the general classification to the photodetectors [18] for ultraviolet
detection.

Table 1.2. General classification of ultraviolet photon detectors

Although UV radiation covers a wide wavelengths, from the extreme ultraviolet (100-10
nm) to near ultraviolet (400–300 nm), the interest here is in reference to optical detector
at ultraviolet (UV) radiation in the wavelengths range 200 – 300 nm, denoted mid
ultraviolet. Meanwhile wavelengths in 100 nm to 200 nm are recognized as far
ultraviolet. The Earth atmosphere mostly absorbs radiation at wavelengths below 300 nm
mainly by ozone (O₃), while oxygen (O₂) is more absorbent in the 100 nm to 250 nm
region. This means that no only astronomy or astrophysics can be find ultraviolet
detectors also terrestrial applications are available to detect UV (i.e. UV emissions from flames, fire backgrounds or security systems). The focus in this thesis is photoelectric detectors using CVD-diamond as a transducer through photoconductive and photo-emissive optical detectors such will be seen in the chapters 2 and 3.

1.3. Gas Sensors

Carbon materials at nanoscale features are to date an ideal component for sensor technology. The great advantage is due to low dimensionality of the structures (offer high specific surface area), allowing more atoms exposure to the environment, therefore the detection sensitivity is high. In general, the conventional gas sensors rely on measuring the change of an electrical quantity of the active material inside of the sensor. This change is attributed to adsorption or absorption of chemical species at the surface of the active material. Transduction properties mainly are in function of carrier mobility and low noise characteristics. Carbon nanotubes and graphene are the best examples of the ballistic charge transport, their electrical resistance could be reversibly tuned by exposure to small gas concentration, so carbon nanomaterials are amenable to usable in gas sensor devices as will be seen in the chapter 4.

The class of gas sensor more representative is based on metal-oxides (MO). The adsorption of some gases, toxic pollutants (CO, H₂S, NOₓ, SO₂, etc.), on MO (e.g. SnO₂) surface is good and can be enhanced by doping process with different additives for example palladium or platinum.
1.4. Research goals

After mastering the synthesis and characterization of bamboo-like carbon nanotubes (B-CNT) and CVD-diamond materials, the research was focused on the assessment of their sensitivity and capability as base materials for gas and ultraviolet sensor detectors, respectively. This thesis undertook the development of the potential applications at room temperature for both diamond and CNTs. In particular, in this thesis, the following three research goals were accomplished:

- Sulfur enhances the photoconductivity characteristics in polycrystalline and nanocrystalline diamond films.
- Tin dioxide-based gas sensor normally can operate at ~100°C. However B-CNT possess chemical and physical properties that allows to tin dioxide-based sensor operate at room temperature with excellent response.
- B-CNT here synthesized can be conformal coat with functional oxides uniformly at high temperature and under an oxygen atmosphere.
REFERENCES


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   - Properties of Carbon and C60 – http://www.creativescience.org.uk/propc60.html
   - Physical Properties of Carbon Nanotubes http://www.pa.msu.edu/cmp/csc/ntproperties/


Chapter 2

Ultraviolet photosensitivity of sulfur-assisted micro- and nano-crystalline diamond

2.1 Introduction

There is a great deal of interest in the development of ultraviolet (UV) sensors for environmental studies and astronomy. UV detectors will have a wide range of applications, such as: (i) monitoring of UV radiation flux on the earth surface, (ii) detection of fires, (iii) monitoring of combustion processes, and (iv) study the evolution of galaxies. These applications require UV sensors with long term stability, high sensitivity and fast response rate. Diamond is a good candidate for robust, solar-blind UV sensors due to its wide band gap energy around 5.5 eV, chemically inertness and radiation hardness [1, 2, 3].

Jackman et al. [4] are pioneers in diamond-based UV sensors. They have reported studies on the potential of CVD diamond photoconductive structures, and evaluated different parameters like responsivity, photocurrent, and quantum efficiency as a function of time [5]. Several research groups have developed UV sensors using diamond films [2, 6, 7]. In particular, Uchida et al. [8] demonstrated that diamond UV sensors have high stability during long term exposure to UV radiation. In contrast, silicon-based UV sensors [9]
commonly used for UV radiation monitoring become significantly degraded, especially when they are used for measurements of continuous UV radiation.

Photosensors based on natural and synthetic diamond are blind to visible and near UV radiation but are sensitive with respect to vacuum ultraviolet (VUV) radiation. Hayashi et al. [10] reported an investigation related to possibility of developing of VUV sensors using highly oriented diamond (HOD) crystals. Moreover, using a HOD polycrystalline boron-doped diamond film, Ben Moussa et al. [11] and Lagomarsino et al. [12] developed a sensor with high geometric resolution of 16-20 mm², and Sio et al. [13] carried out studies related to UV sensor size miniaturization.

In this study, we report the UV photosensitivity of sulfur-assisted micro-, submicro- and nano-crystalline diamond films synthesized by Hot Filament Chemical vapor Deposition (HFCVD). Time resolved and steady state UV measurements were done, and compared to the dark and visible light response levels.

### 2.2 Experimental Section

#### 2.2.1 Sample Fabrication

For diamond deposition, the sulfur-assisted HFCVD method [14, 15] was applied in the present study. Micro- (MCD), Submicro- (SMCD) and Nanocrystalline (NCD) Diamond films were deposited on the silicon substrates in HFCVD reactor using different experimental conditions, in the Table 2.1, the experimental parameters controlling the
diamond deposition process were variable. The deposited diamond films were characterized by Table 2.1. Experimental parameters for diamond deposition with the sulfur-assisted HFCVD. The samples were deposited on silicon substrates during 3 hours for 100 sccm flow of the gas mixture at total gas pressure of 20 Torr. The Rhenium filament was heated up to ~22.

<table>
<thead>
<tr>
<th>sample</th>
<th>Substrate temperature</th>
<th>Average grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD</td>
<td>~ 450°C</td>
<td>~ 1.8 µm</td>
</tr>
<tr>
<td>SMCD</td>
<td>~ 650°C</td>
<td>~ 0.5 µm</td>
</tr>
<tr>
<td>NCD</td>
<td>~ 770°C</td>
<td>~ 0.1 µm</td>
</tr>
</tbody>
</table>

different physical methods of XRD (Bruker-12000), Visible Raman Scattering Spectroscopy (Yvon T-64000 spectrometer with Argon-ion fluency laser operating with 514.5 nm wavelength and output power density of about 0.5 kW cm$^{-2}$ with the probing area of about 2 m²), EDS (EDAX - 300), and diamond films of interest were also visualized using SEM images obtained using Scanning Electron Microscopy (SEM) (JEOL Model 35 CF).

2.2.2 Sample characterization

The SEM images were obtained for MCD, SMCD and NCD films, we can see the morphology, and the films have polycrystalline structure where grain size is dependent of experimental conditions of diamond film deposition. Average grain size of diamond
represented in Figure 2.1-(a) is approximately in the ~0.8 - 1.0 µm range (MCD), averaged grid size of diamond polycrystals shown in Figure 2.1 – (c) is in the ~0.14 to 0.3 µm range (SMCD), image represented in Figure 2.1-(b) cannot properly be analyzed due to limitation in SEM method resolution, however it can be noted that average grid size in this case is much less than respective parameter measured for sample shown in Figure 2.1-(c).

XRD patterns were measured for MCD and NCD, are related to typical polycrystalline
diamond film with diamond (111) at 44.08° and (220) at 75.6° peaks. At the bottom in Figure 2.1-(d) MCD, SMCD and NCD films Raman spectra demonstrate characteristics diamond bands. The NCD is normally attributed to 1140 cm\(^{-1}\) band.

![SEM micrographs of MCD, NCD, and SMCD films deposited on Si substrates.](image)

**Figure 2.1.** SEM micrographs of MCD (a), NCD (b) and SMCD (c) deposited on the Si substrates. Images were scanned at the same amplification scale bar within 1 \(\mu\)m. (d) below appears the characteristic Raman spectra of the MCD, SMCD and NCD films.
An amorphous carbon phase is located around of 1596 cm\(^{-1}\). Band with low intensity located around of 1338 cm\(^{-1}\) is also related to diamond (NCD). For MCD film, sharp D-band located around of 1332 cm\(^{-1}\) and G-band located around of 1480 cm\(^{-1}\), SMCD is relative to MCD but less intensity.

**Figure 2.2.** Schematic representation of the device used, building in our lab. The sample is installed on a stand with Al electrodes and then is taken into the cell that is at a pressure ~10^{-3} Torr, room temperature.
Photosensitivity of materials MCD, SMCD and NCD, was studied using device, schematic representation of which is shown in Figure 2.2.

Device consist cross-electrodes, made from aluminum. Both electrodes are connected to the sample surface. Electric potential (9 V) is applied to electrodes like bias voltage. In the steady state experiments, the high pressure Xe lamp 1000 Watts (Oriel Instruments Model 66020) was used. Analog signal from preamplifier goes to input channel of Computer Interface (Stanford Research, SR-245), which is triggered by Digital Delay Generator (Stanford Research, DDG-535). Digital code from Computer Interface is transformed to PC Computer by RS232 serial port using Commercial Stanford Research Software Pack. Each point of the collected signal was averaged by 10 trigger pulses. In the time resolved experiments, the KrF ($\lambda_{\text{exc}} = 248$ nm) and ArF ($\lambda_{\text{exc}} = 193$ nm) excimer lasers (Lambda Physics, Compex-205) were used. Time duration of laser pulses is about 20 - 30 ns. Maximum averaged energy of laser radiation is 248 and 415 mJ/Puls, respectively. Pulsed output signal from device shown in Figure 2.2 was passed to the input channel of digital oscilloscope (LeCroy, WaveSurfer Model 400).

2.3 Results and discussion

Steady state experiments were carried out using high pressure Xe lamp ($\lambda = 255$ nm). The photoconductivity response of the samples of interest was studied as a function of distance between sample surface and radiation source. The “dark” current on samples were around ~10^{-8} amps at a bias of 9 V. In the case where the distance is 30 cm between sample surface and radiation source, signal was measured in both cases - presence of
glass filter with passing band of $\lambda_{\text{pass}} > 320$ nm, and total Xe lamp radiation. Obtained output signal values are 6.1 $\mu$A for all samples with filter, and 54 $\mu$A, 10 $\mu$A and 20 $\mu$A, respectively for MCD, SMCD and NCD without filter in the same distance. These data demonstrate that photo induced conductivity effect is much higher for total Xe lamp radiation, when UV radiation with $\lambda < 320$ nm interacts with substrate surface as well as effect increases from MCD to NCD, also measured for distance dependence of signal of interest is shown in Figure 2.3, from which it can be seen that signal amplitude is reduced with distance increasing. The fitting curves are also represented in the Figure 2.3. The respective dependences represented in coordinate system of $S_{\text{Ph}} \propto d^{-2}$ with a good accuracy can be fitted by linear functions represented in form

$$S_{\text{Ph}}(d, \lambda) = U_{\text{Ph}}(d, \lambda) - U_{\text{Dark}}$$

where $U_{\text{Ph}}(d, \lambda)$ is the photo induced signal, $U_{\text{Dark}}$ is measured "dark" signal. It means that for considered fluency range, system response is linear according to fluency amplitude. Note that the used electronic scheme allows to obtain output signal in the $S_{\text{out}} = 25$ $\mu$A range by UV-illumination lamp, while for data represented in the literature, see the Table 2.3, the range of interest is limited by $\sim 10^{-10}$ A. It means that in our case the obtained Crystalline Diamond (CD) materials and used measurement scheme allow to increase output signal of system of interest at least in $10^3$ times, and S-assisted MCD, SMCD and NCD films can be considered as a good candidates for commercial UV sensors. We weighed out simplest estimations related to photosensitivity of the samples, if we are taking into account that surface area is 1 cm$^2$ and distance between lamp and sample is 30 cm, we obtained sensitivity value in volts units of 11.4 mV (MCD), 21.2 mV (SMCD) and 39.7 mV (NCD) per $4.5 \times 10^{10}$ sec$^{-1}$, if we take into account linear response of the
studied materials on fluency intensity, we can represent sensitivity as follows: $4.0\times10^9$ sec$^{-1}$mV$^{-1}$ (MCD); $2.1\times10^9$ sec$^{-1}$mV$^{-1}$ (SMCD); $1.1\times10^9$ sec$^{-1}$mV$^{-1}$ (NCD).

**Figure 2.** Photo induced conductivity of samples of interest as a function of distance between substrate surface and Xe lamp.
Data sensitivity of MCD, SMCD and NCD is slightly different. Meanwhile on the other hand, time resolved experiments were carried out using radiation of the KrF and ArF excimer lasers, in which the duration time of the optical pulse of such lasers was about 20-30 ns. The waveforms measured for samples of interest for both 248 and 193 nm wavelengths are shown in Figures 2.4 (a), (b), respectively. The decay section of the observed signals can be fitted by biexponential function of

\[ S_{Ph}(t) = S_{Ph1}\exp(-t/\tau_1) + S_{Ph2}\exp(-t/\tau_2) \quad (2) \]

where fitting parameters of \( 1/\tau_1 \) and \( 1/\tau_2 \) are represented in Table 2.2 for all cases of studied. The scale of the \( 1/\tau_1 \) value is practically the same for all samples of interest and for both fluency radiation wavelengths used in the present study. Also \( 1/\tau_2 \) value is practically the same for samples tested by the same fluency radiation, but for different fluency radiation, such parameter value differs at least two times, thereby constituting a useful characteristic according to technological applications. Now if for laser radiation power 1 mJ, number of radiation quanta is determined by the values of \( 1.4 \times 10^{15} \text{ sec}^{-1}\text{mJ}^{-1} \) and \( 1.1 \times 10^{15} \text{ sec}^{-1}\text{mJ}^{-1} \) for 248 and 193 nm radiations, respectively. Thus, we can estimate number of radiation quanta interacting with sample surface as follows: \( 1.6 \times 10^{9} \text{ sec}^{-1}\text{mJ}^{-1} \) and \( 1.2 \times 10^{9} \text{ sec}^{-1}\text{mJ}^{-1} \) for 248 and 193 nm radiations, respectively. Measurable signal can be observed at few mille-joules radiation power, and represented estimations of the material UV photosensitivity is shows that such materials can be considered as a good source for development of a new UV photo sensors. The represented above analysis demonstrates the characterization of the UV photosensitivity properties of materials of interest and can be compared with the work performed by different authors as Mazzeo et.
Figure 2.4. (a) Time resolved photo-response of the MCD, SMCD and NCD samples on pulsed fluency radiation of 248 nm at pulse energy of about 30.3 mJ and (b) Time resolved photo-response of the MCD, SMCD and NCD samples on pulsed fluency radiation of 193 nm.
al. [16], Jackman et al. [17], Ciancaglioni et al. [18], Ralchenko et al. [19], Hayashi et al. [20], which studied response rate of different CD materials obtained by regular CVD method. It has been found by these authors that response time of the materials of interest is in a few nanoseconds time range or simply in seconds. The S-assisted CD materials obtained and tested in the present study have more longer response time (see Table 2.2) and decay time is (~0.2 µs), but we have to note that values of $1/\tau_1$ represented in Table 2.2 can be considered as a lowest limit of the respective response rate despite duration of the laser pulse is about 20 - 30 ns, and real response rate can have much larger value, which is undesirable for a specific application in sensors, as for example UV laser sensor monitor.

**Table 2.2.** Decay parameters of the time resolved photo-response of samples of interest for fluency radiations of 248 and 193 nm.

<table>
<thead>
<tr>
<th>$\lambda_{\text{exc}}$ = 248 nm</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>MCD</td>
<td>SMCD</td>
</tr>
<tr>
<td>$1/\tau_1$ (µs$^{-1}$)</td>
<td>24.37 ± 0.73</td>
<td>24.06 ± 0.68</td>
</tr>
<tr>
<td>$1/\tau_2$ (µs$^{-1}$)</td>
<td>5.29 ± 0.32</td>
<td>4.83 ± 0.44</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\lambda_{\text{exc}}$ = 193 nm</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>MCD</td>
<td>SMCD</td>
</tr>
<tr>
<td>$1/\tau_1$ (µs$^{-1}$)</td>
<td>28.14 ± 0.76</td>
<td>28.66 ± 0.66</td>
</tr>
<tr>
<td>$1/\tau_2$ (µs$^{-1}$)</td>
<td>9.60 ± 0.41</td>
<td>10.10 ± 0.45</td>
</tr>
</tbody>
</table>
In our experiments, very probably, some effect of sulfur can be expected like electronic transitions in S-assisted diamond films can be induced by radiation with longer wavelength, of which is about 248 nm. The S atom may significantly shift absorption band of materials of interest to "red" spectral area. For samples studies in our case difference of material photosensitivity according to radiation with $\lambda > 320$ nm and total Xe lamp radiation is between 10 to 40 times range as well as an external quantum efficiency is low ($\eta \sim 0.5$) than represented by other authors such as Koide et al., Almaviva et al. Although materials investigated in our study do still not comparable by sensitivity properties with devices actually developed and studied by Bevilacqua and Jackman [0], although materials obtained and tested in our study have very promising sensitivity properties especially according to photocurrent resolution whose values are comparable appreciating to the Table 2.3. Also some studies have concentrated attention on very far VUV radiation (i.e. see last line in the Table 2.3), and the observed by them effects can directly not be correlated with data represented in our study, however, we may note that photosensitivity properties of diamond films overlap region from regular UV to very far VUV radiation. The measurements presented in this paper suggest that the sensitivity of the diamond film between them is not significantly different from one another, Fig.5. Such effect can apparently be related to difference of absorption cross sections of diamond film sample for both radiation wavelengths (also Xe lamp irradiation) as well as such effect may be result due to difference between diamond film samples and measurement scheme used in both cases. It should also be noted (Table 2.3) that in the literature many studies are related to investigation and development of UV photosensors based on diamond film materials in where the samples are definitely different.
Figure 2.5. Comparison of photocurrent measured in NCD, SMCD and MCD from "dark" current (~10^{-8} A) until illumination mode using different sources like a UV-illumination (Xenon Lamp) and pulse width 20 to 30 ns laser irradiation (ArF and KrF). Also is possible observe the signal under source of visible radiation.
**Table 2.3.** Photocurrents detected by different authors. Compare the type of sample and the sensitivity region. The measurements were performed at room temperature in a vacuum system.

<table>
<thead>
<tr>
<th>Type</th>
<th>Decay time</th>
<th>Photocurrent</th>
<th>Region</th>
<th>Authors and Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>CVD-MCD</td>
<td>5 s</td>
<td>~ $10^{-10}$ A</td>
<td>R.B. Jackman et al. 1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~ 0.12 A</td>
<td></td>
</tr>
<tr>
<td>Undoped</td>
<td>HO-MCD</td>
<td>5 ns</td>
<td>(under high bias)</td>
<td>K. Hayashi et al. 2001</td>
</tr>
<tr>
<td>S-doped 8×10^{12} cm^{-3}</td>
<td>CVD-MCD</td>
<td>None</td>
<td>~ $10^{6}$ a.u.</td>
<td>E. Gheeraert et al. 2002</td>
</tr>
<tr>
<td></td>
<td>MWPECVD-diamond</td>
<td>3 s</td>
<td>~ 5 pA</td>
<td>Donato et al. 2006</td>
</tr>
<tr>
<td>B-doped 10^{16} cm^{-3}</td>
<td>CVD-MCD</td>
<td>20 s</td>
<td>~ $10^{-11}$ A</td>
<td>Koide et al. 2007</td>
</tr>
<tr>
<td>N-doped 10^{14} cm^{-3}</td>
<td>MPACVD</td>
<td>10 s</td>
<td>~ 700 pA</td>
<td>A. Secroun et al. 2007</td>
</tr>
<tr>
<td>N-doped</td>
<td>MPACVD-UNCD</td>
<td>3 s</td>
<td>4×$10^{-4}$ a.u.</td>
<td>M.C. Feliciani et al. 2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~ 10 pA</td>
<td></td>
</tr>
<tr>
<td>Undoped</td>
<td>CVD-NCD</td>
<td>None</td>
<td>~ 1 pA</td>
<td>Remes et al. 2008</td>
</tr>
<tr>
<td>Undoped</td>
<td>CVD-MCD</td>
<td>None</td>
<td>~ 4×$10^{-8}$ A</td>
<td>T. Kubo et al. 2009</td>
</tr>
<tr>
<td></td>
<td>homoeptaxial</td>
<td>None</td>
<td>~ $10^{-10}$ A</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~ 4×$10^{-8}$ A</td>
<td></td>
</tr>
<tr>
<td>B-doped</td>
<td>CVD-MCD</td>
<td>None</td>
<td>~ $10^{-11}$ A</td>
<td>T. Kubo et al. 2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~ 4×$10^{-11}$ A</td>
<td></td>
</tr>
<tr>
<td>Undoped</td>
<td>HFCVD-MCD</td>
<td>None</td>
<td>~ 65 µA</td>
<td>K. Tang et al. 2009</td>
</tr>
<tr>
<td>B-doped</td>
<td>MWPECVD-MCD</td>
<td>&lt;1 s</td>
<td>~ $10^{-12}$ A</td>
<td>S. Almaviva et al. 2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~ 3×$10^{-12}$ A</td>
<td></td>
</tr>
</tbody>
</table>

27
We can see, considering Table 2.3, our samples photo response is high, and in this case it is reasonable to propose that relaxation process of intermediate species, due to S-atom and D-defect in the samples, are more quickly developed than in case of B and N atoms CD doped, the analysis of phenomenological model (photocurrent theoretical point of view) explains this aspect, which is widely represented in the literature i.e, [16, 21, 22, 23, 24, 25]. In few words, these authors developed model in which the electron-hole pairs are photo generated by the light radiation (UV region) in the diamond film recombine either directly or through defect states acting as recombination centers. We apply the numerical analysis in our context problem of interest and were carried out for phenomenological parameter whose system photoresponse was calculated as function of S-atoms [N_S] and D-defects [N_D] concentrations using Runge-Kutta [26] approximation method. The concentration of S-atoms and D-defects were varying in the $10^{16}$ - $10^{19}$ cm$^{-3}$ and $10^{15}$ - $10^{18}$ cm$^{-3}$ ranges, respectively. It can be seen for both dependences of interest that with increase of S or D concentration, relative current initially increases and then it decreases, for example both dependences of interest have maximum photoresponse value. Thus, according to analyzed model we can assume that the photo induced current can be optimized by variation both S and D concentrations. Such dependences can qualitatively be understood using the proposed mechanism. With increase either S or D concentrations, the electrons and holes are stabilized by trapping effects of these species by S or D, inverse processes of such intermediate decomposition induce formation of free electrons and holes, such intermediates can be considered as accumulators of free electrons and holes. Further, increase of concentrations of S or D induces effective recombination processes of intermediates of interest. The last recombination effect reduces the relative
photocurrent on the system, so we found that concentrations of sulfur equal to \([N_S] = 3 \times 10^{16} \text{ cm}^{-3}\) when the concentration of defects is \([N_D] = 3 \times 10^{17} \text{ cm}^{-3}\) yield a maximum value (arbitrary units) in the photo-response system.

### 2.4 Conclusions

In the present study, it was shown that sulfur-assisted MCD, SMCD and NCD have very promising UV photosensitivity properties. The estimated sensitivity of materials of interest is in the \(10^9 \text{ sec}^{-1} \text{ mV}^{-1}\) range, and time resolution with respect to the UV radiation of such materials is better than 100 ns. For spectral range of \(\lambda > 320 \text{ nm}\), the tested materials are solar blind. S-assisted MCD, SMCD and NCD can be used for the long time monitoring at the environment and in aerospace applications.
REFERENCES


Chapter 3

Ultraviolet photoconductivity and photoelectron field emission characteristics of sulfur-assisted crystalline diamond films

3.1. Introduction.

The widely discussed Chemical Vapor Disposition (CVD) diamond physical properties are still of interest for the fabrication of ultraviolet detection devices [1,2,3]. An important condition for these diamond detectors is to achieve significant responsivity or photocurrent despite the weak signal detection such as chemical sensing or optical windows with reduced pixel size.

Electrical properties of the diamond are have been achieved by defects and impurities, which are electrically active elements present in grain boundaries [4]. These boundaries are covered with hydrogen-termination and non-diamond phases applying different strategies. For example, hydrogen on a polished diamond surface [5] produce holes near the diamond’s surface creating a high density conductive layer (p-type). H-termination in diamonds forms heteropolar C-H bonds yielding H with a negative charge (surface side) and C a positive charge (film side) in such that the work function is reduced. This results in a negative electron affinity (NEA) [6], ideal for field emitters at -1.27 to -2.07 eV for a
hydrogenated [7] diamond and 0.38 to 0.69 eV for clean [8] diamond. The NEA value was theoretically and experimentally assessed by Amit et al. [9]. Indeed, undoped type IIa-diamond also is conductive by hydrogenation methods and exposure to the environment [10]. In general, NEA is induced by hydrogen termination in diamond surfaces or synthesized by (CVD) in undoped or doped diamonds offering all manners of electron emission current. This quality strengthens the fabrication of UV radiation detectors, such as solar blind detectors and cold cathode emitters [11, 7]. Studies performed by Kalish et al. [12] show how the electron field emission from undoped type IIa-diamonds, whose surface has been rendered conductive by transfer doping (NEA induced), is enhanced by visible light illumination (photon-excitation).

Other studies [13] demonstrate that grain boundaries, in the case of CVD-diamond, are considered a major source of conductive contributions with high density of sp²-bonded carbon atoms residing at the grain boundaries. These diamond films show a significant electrical conductivity and electron field emission.

In this study, we fabricated sulfur assisted-diamond films grown by hot filament chemical vapor deposition (HF-CVD). The incorporation of impurities in the diamond material can improve the responsivity. Gupta et al. [14, 15], incorporate sulfur into the diamond film samples (n-type dopant, 0.37 eV of activation energy [16]) via the addition of hydrogen sulfide (H₂S) gas to the conventional (CH₄/H₂) gas mixture to investigate if S-assisted diamond can help to control and may enhance the electron field emission properties of microcrystalline diamonds and nanocrystalline carbon films.
Room temperature field-emission measurements at low electric field (0.7V/µm to 1.7V/µm) were carried out to assess the photoresponse of the S-assisted samples. While the samples were illuminated by ultraviolet radiation. In a previous publication, we describe the performances of a photodetector based on HF-CVD sulfur assisted-diamond using a planar configuration [17] in which diamond surfaces were verified as a reliable ultraviolet detector in planar configuration within a nano-scale time at low persistent photoconductivity effect (PPC) [18]. In this paper, we aspire to demonstrate that FE configuration diamond detectors have a more sensitive response to UV radiation in the range 200 nm to 300 nm compared with the planar configuration when applied on the different diamond samples.

3.2. Experimental details

3.2.1. Sample Fabrication

During diamond deposition, the sulfur-assisted HFCVD method [19, 20] was applied in the present study. The films were deposited on silicon oxide substrates in HFCVD reactor using different experimental conditions. The hot filament system used in this experiment was a customized CVD reactor for diamond deposition. The standard procedure of diamond deposition can be found elsewhere in this reference [19]. Briefly, the substrates were heated up to 700–900°C over a time period of 3 hours and run with a chamber pressure of 20 Torr at 2% of methane diluted in hydrogen (CH₄/H₂) and 500 ppm of sulfur diluted in hydrogen. Tungsten filament (0.05mm diameter) was placed horizontally and heated up to ~2000 °C to decompose the hydrocarbons gas mixture. For this
experiment, we obtained grain sizes 3µm, 0.5 µm and 0.1µm for samples micro- (MCD), submicro- (SMCD) and nanocrystalline (NCD) diamond respectively.

3.2.2. Sample characterization
The deposited diamond films were characterized by different physical methods such as Visible Raman Scattering Spectroscopy (Yvon T-64000 spectrometer with Argon-ion fluency laser operating on a 532 nm wavelength and output power density of about 5 mW/cm² with the probing area of about 2mm²), EDS (EDAX - 300), and diamond films of interest were also visualized using Scanning Electron Microscopy (SEM), JEOL Model 35 CF.

3.2.3. Measurements
Figure 3.1, depicts two kind of measurements used in this experiment: time and wavelength dependence measurements. The purpose of time dependence measurements was to identify the response and photosensitivity behavior on diamond films for different ultraviolet sources such as excimer lasers with fixed values (ArF =193 nm and KrF =248 nm). The laser pulses were released among 20 - 30 ns at 10 – 30 mJ of energy. The measurement of the data was recorded following the procedure described elsewhere in the reference [17].

The second experiment, wavelength dependence, was carried out to identify the spectral response of the samples in the presence of tunable UV radiation inside a range 200 - 300 nm, at scanning stepwise of 1 nm. The system was implemented through an emission spectrum of Coumarine-47 at 3-5 mJ of energy.
Figure 3.1. Diagram of two experimental arrangement, the time and wavelength dependence measurements.

(a) Photoconductive mode

(b) electron field emission mode (EFE)

(c) Photo assisted EFE

Figure 3.2. Diagrams of the configuration used for the electrodes connection in the samples in a) planar configuration, b) Field Emission configuration and c) the simplified version of diagram b).
Figure 3.2 contains two diagrams of the configuration used for the electrodes connection in the samples. Figure 3.2-(a) shows the planar configuration (PC) which consists of two biased aluminum electrodes (at 9 V) on top of the samples. The main idea is to produce an external current (photoconductive current), between the electrodes, induced by UV radiation. The device shown in the figure is based on a system previously elaborated in an article written by our lab team and is mentioned within the references [17].

In order to understand the behavior of our samples, we evaluated their responsivity to ultraviolet light, following the method referenced [21]. The spectral responsivity was measured in parallel with a calibrated photo-diode and expressed in amperes per watt. Here, the responsivity of the diamond ($R_d$) was evaluated by comparing the photocurrents measured by the photo-diode ($I_p$) and those measured by the diamond ($I_d$).

$$R_d = R_p \frac{I_d}{I_p}.$$  \hspace{1cm} (1)

In general, responsivity ($R_i$) obeys to the determination of quantum efficiency ($\eta$) and photoconductivity gain ($g$) evaluated in a photodetector. On the other hand, $R_i$ spectral [22] can be obtained from $R_i = \frac{\lambda \eta}{hc} qg$ in which $\eta$ represents the number of electron-hole pairs generated ($I_{ph}/e$) per incident photons ($P_i/h\nu$). $\lambda$ is the incident wavelength, $h$, $c$, and $q$ are the constant values Plank, light velocity and electron charge respectively. Also, to determine an estimation of the external quantum efficiency we can use the following relationship:

$$\eta = \frac{I_{ph}/e}{P_i/h\nu}.$$  \hspace{1cm} (2)

In the other configuration, the Figure 3.2-(b) and the simplified version in Figure 3.2-(c), consist of a field emission mode used to detect the current emission induced by UV-
photons. One feature of the field emission configuration is the presence of a vacuum-space between the diamond surface and the anode (see diagram detail on Figure 3.2-(c)) to which is applied a specific voltage (electric field). In this case, the diamond film (sensitive area of ~15 mm$^2$) is part of the electrode as the cathode is slightly separated (30 µm of Teflon gasket) from the other electrode known as the anode. The anode consists of a copper ring measuring 5 mm in diameter. During the measurements, the electrodes were biased with different voltages (20, 30, 40, and 50 V) to observe possible changes in the response such as reproducibility and stability of the signal. In our experiment the lowest biases maintained the threshold electric field at 1.8 V/µm, taking in to account that 2.2 V/µm is the threshold value for nano-diamond films case. The emission current was measured in terms of the wavelength with was between 200 to 300 nm. The general idea was to examine the current switch optically by ultraviolet means.

Theoretically, a model that better explains the ejection of electrons from the surface to the vacuum is the Field Emission Theory [23]. The model expounds that the emission current (current density ($J$)) depends on different factors; one of the most important is the quantity of electrons available on the sample surface ($f$). A second factor is the escape probability ($P$) of an electron from an energy level into the vacuum to overcome the height of the energy barrier ($U$) in order to reach the other electrode. So

$$J(F) = \frac{1}{2\pi} \int_0^\infty \frac{\hbar k}{m} P(\varepsilon_i)f(\varepsilon_i) d\varepsilon_i$$  \hspace{1cm} (3)

$f$ also represents a density of carriers in a particular energy level ($i$), near the surface. In the presence of an electric field (or biased electrodes), but without illumination on sample
(photo-excitation), the probability of the electrons escape \( (P_0) \) can we assume by the following equation [25]

\[
P_0 = e^{-\frac{4\sqrt{2m}\phi}{3hF}(U-E_0)^{3/2}}
\]  \( (4) \)

In which \( F \equiv E (\text{eV}/\mu\text{m}) \) an applied field, \( U \) is the barrier height \( \phi + \mu \), where \( \phi \) (eV) is a work function, and \( \mu \) (eV) is a chemical potential, and \( E_0 \) is the ionization energy.

However, all contributions can be gathered as a surface potential like a general approximation. In the presence of light on sample, \( E_0 \) energy increases and becomes \( E_0 + h\nu \) so

\[
P_1 = e^{-\frac{4\sqrt{2m}\phi}{3hF}(U-E_0-h\nu)^{3/2}}
\]  \( (5) \)

If we will take into account electron affinity \( \chi \) in the presence of light, \( E_0 + \chi \) energy increases and becomes \( E = E_0 + \chi + h\nu \) and

\[
P_1 = e^{-\frac{4\sqrt{2m}\phi}{3hF}(U-E_0-\chi-h\nu)^{3/2}}
\]  \( (6) \)

It follows that \( P_0 < P_1 \) and with increase of \( F \) (electric field) \( P_0 \rightarrow P_1 \). Therefore

\[
\frac{P_1}{P_0} = e^{-\frac{4\sqrt{2m}\phi}{3hF}\left[(U-E_0-\chi-h\nu)^{3/2}-(U-E_0)^{3/2}\right]}
\]  \( (7) \)

in which \( \chi \) is the electron affinity of the semiconductor as a negative value in the case of a hydrogenated diamond film. Therefore, the sources of the electron emission are associated with reduced values of the work function; therefore surface samples are easily conductive upon UV irradiation [9].
3.3. RESULTS AND DISCUSSION

3.3.1. Material configuration

The scanning electron microscopy, in Figure 3.3 (a), shows polycrystalline structures of different average grain sizes. We observe a MCD diamond has an average grain size of ~1.0-3.0µm, a SMCD diamond averages a grain size of ~0.2 to 0.5 µm, and in the case of a NCD diamond an average grain size of less than 0.1 µm. Figure 3.3 (b) shows the Raman spectra of microcrystalline S-assisted and undoped diamond thin film. This was done in order to corroborate changes around the region of 1560 cm$^{-1}$ (G-band) for both undoped and doped samples. The G-band (sp$^2$ content) is notable in sample S-assisted. At 1332 cm$^{-1}$ the diamond (sp$^3$) reaches its peak performance; this performance remains similar for both undoped and S-assisted cases. Figure 3.3 (c) represents the comparison of the MCD, SMCD and NCD films on the Raman spectra. For the MCD film, there is a sharp D-band located around 1332cm$^{-1}$ and a G-band located around 1480 cm$^{-1}$. The SMCD is relative to MCD but has less intensity. The NCD is normally attributed to the 1100 - 1140 cm$^{-1}$ band. An amorphous carbon phase is located around 1580-1660 cm$^{-1}$. The D-band in the NCD has low intensity located at 1338 cm$^{-1}$. The role of the different grain sizes is to promote differences in the density of point defects (i.e. grain boundaries) which in turn produce electrical effects in the photoconduction phenomena. Meanwhile, when the grain size decreases, the quantity of sp$^2$ C-rings increases [26], which means that the non-diamond phase is interconnected with the diamond grain size. Adding sulfur during CVD process enhances the formation of non-diamond carbon [15] which is observable in the Raman spectra, Figure 3.3 (b). The presence of the intentional impurities, incorporated in diamond samples is interpreted as changes in the crystalline
quality and changes in the structural characteristics of the diamond (specially around G-band), as we saw.

![Figure 3.3.](image)

**Figure 3.3.** Optical images from scanning electron microscopy (SEM) with a) polycrystalline structures of different average grain sizes, b) the Raman spectra of microcrystalline S-assisted and undoped diamond thin film and c) the Raman spectra of MCD, SMCD and NCD samples.
3.3.2. Performance of photoconductive planar configuration on diamond samples

Figure 3.4 shows the performance response of the samples in nanoscale resolution time. The graph represents the tests done to the samples in planar configuration below KrF (248 nm) and ArF (193 nm) excimer laser. We observe that the material has 100 ns of effective time response at 9V of bias applied between electrodes. Two parts are emphasized in the graph; the time-rise saturation and the decay time is in between 30 to 40 ns range. The photocurrent generated in S-assisted diamond across the electrodes, at the same detection region, lasts for a shorter period of time than the conventional undoped diamond surface [27, 28, 29]. Additionally we see a short permanent photocurrent (PPC) during the decay time, and a recovery position on the signal returns to the original position. The diamond film shows similar photocurrent values, reaching micro amps values (~0.8 – 1.2 µA) from the dark current measurement (~ 0.01 µA) at 9V of bias between the electrodes.

The external current formed on samples (photocurrent) was induced by excimer laser. The radiation energy is comparable with the diamond band gap (around ~5.6 eV) which is absorbed by the films; therefore, free carriers are formed and conductivity increases in the material despite the effects from recombination and trapping due to defects, dopants, or absorption cross-sections of the diamond films. The photocurrent signal is enough to generate a detector of ultraviolet light. On diamond surfaces the activation of energy by defects is common predominantly at the grain boundaries ranges (around 240 nm) like conductive channels densely concentrated with sp² [13, 30]. Normally, the interrelation
between sp\(^2\) and grain boundaries is chemically analyzed by the net Electron Energy Loss Spectroscopy (EELS) signal at a nanometer scale. The EELS of carbon atoms is represented by two types of electronic states: \(\theta - \theta^*\) electronic states associated with \(\theta - \text{sp}^3\) domains are characterized by an \(\theta^*\) line \(~290\ \text{eV}\) (band gap), and \(\pi - \pi^*\) states associated with \(\pi - \text{sp}^2\) domains are characterized by an \(\pi^*\) line at \(~285\ \text{eV}\). These suggest that the energy difference between \(\theta^*\) line and \(\pi^*\) line is \(~5\ \text{eV}\) \([31, 32]\).

**Figure 3.4.** Photoresponse in time response of the samples in planar configuration below KrF (248 nm) and ArF (193 nm) excimer laser.
Figure 3.5. Spectral responsivity in the 200 – 300 nm range for the S-assisted diamond surfaces, planar configuration.
The graph in Figure 3.5 summarizes the spectral responsivity in the continuous region between wavelengths 200 – 300 nm for the S-assisted micro, sub-micro and nano diamond surfaces (This was also examined in a previous study, elsewhere in ref [17], at 193 and 248 nm with an ultraviolet source by excimer lasers). In the narrow region of 200-250 nm, we observe features in the spectral responsivity of the samples around of 225 nm (wide absorption range) and 240 nm (single-peak). The graph also shows the behavior of responsivity after 230 nm while it decreases quickly to ~240 nm. Later it is separated by a flat valley from the first peak (225 nm). The samples above 250 nm are not sensitive to spectral UV radiation in the planar configuration. The high values in a photocurrent gain are induced by specific illuminations in 225 and 240 nm inside the spectral responsivity. However, the responsivity decreases due to the fact that the life time charges are at a high level of recombination speed inside the inter-band activity of the CVD diamond during the wavelength changes [5]. The graph is characterized by several peaks, the most notable being the band gap of the diamond material around 225 nm. The other peaks (around 240 nm) represent carrier mobilities, charges localized in point defects and the sample grain size, among other characteristics[33, 4]. The Sulfur-assisted (incorporation of impurities shallow) in our samples produced negative charges near the surface [34]; therefore, sulfur electrical effects also contribute to the external current during the ultraviolet irradiation [35]. Additionally, under planar configuration, it was taken into consideration that the electrodes in the samples generated side effects [36].
Figure 3.6. a) Spectral responsivity in the 200 – 300 nm range for the S-assisted diamond surfaces, Field Emission configuration. b) Schematic of the proposed band diagram for S-assisted diamond surfaces showing band gap, Fermi level (EF), conduction band minimum CB, valence band VB and work function W.
3.3.3. Photo-response in diamond samples through field emission configuration

Figure 3.6 contains the spectral response curves of MCD, SMCD and NCD films below field emission configuration (1.7 V/µm on field) at a wavelength illumination range of 200 to 300 nm. The differences between responses (profile of current emission during the scanning) of the diamond films were observed and marked in three visible regions for each sample (A, B and C). The signal in region (A) appears similar across the three samples, with the same maximum value located in 220 nm. In the next region (B), the emission current decreased for the MCD from 220 nm to 240 nm, meanwhile in the NCD sample the current increased in response. While scanning region (B), the signal in the microcrystalline diamond is lower in comparison with the NCD which is more intense than in region (A). The maximum peak value is shifted in each sample. In the case of region (C), we observe a shoulder with weak signal for NCD compared with the other samples.

The relatively high signal in region (A) (noted in the graphs) is believed to be caused by carriers generated from internal states of the band gap in the material, coming close to 5.6 eV (λ = ~225 nm). The regions (B) and (C) may represent the contribution of non-equilibrium carriers generated by different sources prompted during the illumination. Photocurrent gain was observed during increments of bias voltage applied in the circuit (i.e. 20 to 50 volts), visible changes in the intensity of the current emission signal for the samples of interest. The effects the different grain sizes produce are notable under field emission configuration. For a small grain size, the region (B) in NCD shows an
improvement of the signal between samples. The overall shape of the spectral response
does not depend of the applied bias. We assume, through the low fluctuation rate in
graphs, that thermal effects during the process are not substantially disturbed.

Figure 3.6 (b) in contrast with figure 3.6 (a), is a schematic of the proposed band diagram
for S-assisted diamond surfaces during UV illumination. The figure is showing the band
gap, Fermi level \(E_F\), conduction band minimum CB, valence band VB, work function
W and the most representative energy values activated during the interaction with UV
light. Unlike the performance of photoconductive planar configuration on diamond
samples, here the results show additional values. The observable energy values are at
\(~5.6\) eV (band gap material), \(~5\) eV (graphitic compound) \(\text{sp}^2\) bonded carbon formed in
the grain boundaries \([8]\), \(4.4\) eV represent the NEA surface effect \([37]\) and presumably
\(0.37\) eV up to the band gap shallow S-atoms as donors \((\sim5.97\) eV).

Under the FE configuration, the NCD sample is sufficient to discriminate between two
detectable wavelengths for UV radiation. Usually photodetectors can only detect one
specific wavelength (planar mode). In this article, the FE method provides an interesting
route to perform a device for different spectra selectivity without the integration of other
materials at different band gap. However, FE mode in this case results compositionally
expensive compared with two-terminal device structure.
3.4. CONCLUSION

We performed photo-electrical responses using two detector configurations of sulfur-assisted crystalline diamond films synthesized by hot filament chemical vapor deposition. We reported the ultraviolet photo-response in the range of 200 to 300 nm. The spectral response in our samples was evaluated in a common configuration (planar) and compared with the photo-response under a configuration based in field emission at low electric field values (0.7V/µm to 1.7V/µm). The measurements used to compare the performance of the UV light on the samples contain marked differences for the NCD and MCD films. We found that the external current induced by UV-light (photocurrent) between the biased electrodes of the samples was produced by different electrons sources such as different energy levels the middle of the band gap. During FE mode, the signal depends of the wavelength to activate the current between the electrodes. The emission is stable and reproducible within different low bias voltage values (20 to 50 volts) allowing the possibility to easily switch currents optically at room temperature. Field emission configuration through the electrons that are photo-induced with UV light is improved by the properties of sulfur-assisted crystalline diamond films and an effective grain size, proving an alternative option for diamond based detectors.
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Chapter 4

Room temperature gas sensor based on tin dioxide-carbon nanotubes composite films

4.1. INTRODUCTION

Tin dioxide (SnO$_2$) has been studied by different research groups due to its capacity to adsorb molecules in the gas phase [1, 2, 3] and Li-ions in rechargeable batteries [4, 5, 6, 7], improving the performance of bare CNTs. SnO$_2$ is a n-type semiconductor metal oxide with a band gap of 3.6 eV [8], making it a favorable material for sensing devices [9, 10, 11]. It has applications in environmental problems caused by the emission of pollutants from assorted sources, such as CO, NO$_x$, SO$_2$ [12] and H$_2$S [13], which represent a great concern for public safety.

Hydrogen sulfide is well known in the oil and food industry, and in organic waste in areas such as sewers. In the case of aldehydes, they have important uses in the pharmaceutical and food industry. SnO$_2$ is widely used for alcohol detection, especially ethanol [14]. Although undoped SnO$_2$ gas sensors have low sensitivity and selectivity [15], they can be improved by combining with other materials [16].

Studies demonstrate that carbon nano-materials (CNMs) [17, 18] (i.e., carbon nanotubes, nanobelts, nanowires) are good candidates as potential “dopants” of SnO$_2$. In general,
CNMs influence the materials’ charge transfer, electrostatic environment, surface area, and molecular adsorption [19], thus improving the properties required for gas sensing [20]. Gas sensors based on CNMs in their bare form (without using dopants or hybrid materials) have been shown to detect nitrogen [21], hydrogen [22], ammonia [23], and other gas and vapors [24]. Moreover, their sensitivity can be enhanced by blending with activated materials [18, 25, 26]. However, these sensors conventionally operate at temperatures above ~200°C to obtain reasonable responses [18, 27, 28]. Furthermore, the baseline gases used and analyte concentration affect the response and recovery times [29] of the sensors. Wei et al. [19] combined SnO₂ with single wall carbon nanotubes to develop a gas sensor for NO₂ at room temperature. They reported enhanced sensitivities of the hybrid sensor compared to pure SnO₂, but the response time is long, in the order of minutes. Chen et al. [30] prepared CNT/SnO₂ core/shell structures to measure ethanol gas at various concentrations with a working temperature of 300 °C. The core/shell configuration and working temperature enhanced the sensitivity up to 24.5 at low gas concentrations.

We hereby report the room-temperature sensor characteristics of Tin Dioxide-Carbon Nanotubes composite films. They can detect ethanol, methanol and H₂S down to ppm levels, with excellent response and recovery times at room temperature and ambient pressure.
4.2. EXPERIMENTAL

4.2.1. Material and methods

Figure 4.1 depicts a flowchart of the method used for the synthesis of tin dioxide-carbon nanotubes composite films and a representative electron microscopy image of the product. The films were grown on 14-mm diameter, 0.5 mm thick copper substrates (GoodFellow, 99.9% pure Cu). These substrates were mechanically polished with sand papers down to 2500 grit and cleaned by sonication in methanol. A 2:1 ethanol solution of SnO$_2$ nanopowder (Nanostructure and Amorphous Materials, Inc, 99.5%) and NiO
powder (Alfa Aesar, 99 %) was deposited over the heated substrate until the surface was completely covered and the solvent was evaporated. The coated substrates were then introduced in a custom made HF-CVD chamber which has been previously described in detail elsewhere [31]. The gas mixture consisted of 2.0% methane diluted in H₂. It was flown at 100 sccm and 35 Torr, and kept constant during the deposition time. The composite films were grown at ~700°C for 5 minutes. This deposition time was selected in order to achieve a fully covered film that did not experience peeling or delamination. The surface and nanostructure of the composite films were analyzed by high resolution scanning electron microscopy (HRSEM) with a JEOL JSM-7500F.

4.2.2. Gas sensing procedure

The setup employed for gas detection is shown in Figure 4.2. Nitrogen was used as carrier gas at a flow rate of 100 sccm. Mixtures of 50, 100, 150 and 200 ppm were prepared in advance for each gas: H₂S, C₂H₅-OH and CH₃-OH. The cycles consisted of 100 seconds of wait time followed by 100 seconds of gas detection. Standard gas testing was performed at room temperature, atmospheric pressure, and in N₂ atmosphere with negligible relative humidity. Nonetheless, tests done in open air in the presence of ambient vapor (relative humidity ~ 57 %) showed no significant changes in the sensors’ response, in the 3 – 5 % range. Note also that the devices were exposed to open air prior to testing and we did not apply any special procedure to remove the adsorbed water vapor.
The device used is described in detail elsewhere [32]. Briefly, the device consists of a plastic plate of $2 \times 2 \text{ cm}^2$, to which 4 polished rectangle aluminum electrodes are attached by 4 stainless steel screws. Samples were placed between the plastic plate and aluminum electrodes while the back side substrate surface was attached to plastic the plate surface. Figure 4.3 shows a general representation of the sensor device connections. $R_r$ is the reference resistance and $V_m$ is the measured voltage. A bias voltage ($V_s$) of 3V was constantly applied to the sensor, which behaves as a resistance.

![Diagram of the gas sensing experimental setup.](image1)

**Figure 4.2.** Diagram of the gas sensing experimental setup.

![Diagram of the gas sensing experimental setup.](image2)

**Figure 4.3.** Device configuration for gas sensing.

![Diagram of the gas sensing experimental setup.](image3)
The most common model \cite{13, 33, 34} of gas sensing mechanism for metal oxide-based sensors involves adsorption, reaction gas-surface, and desorption. In order to understand the behavior of our sensors we measured their sensitivity toward to analytes, following reference \cite{19}, as the ratio between the change in relative resistance ($\Delta R$) and the change in the concentration ($\Delta C$) of the desired gas (analyte), using the following equation:

$$Sensitivity = \frac{R_{\text{analyte}}}{R_{\text{line}}} = \frac{\Delta R}{\Delta C}$$  \hspace{1cm} (1)

Where $R_{\text{line}}$ and $R_{\text{analyte}}$ represent the electrical resistance of the device in pure N$_2$ and in the mixture of N$_2$ plus the analyte, respectively. The values of $R_{\text{line}}$ and $R_{\text{analyte}}$ are obtained through by the following relationships:

$$R_{\text{analyte}} = R_r \times \frac{V_s - V_{\text{analyte}}}{V_{\text{analyte}}} \quad \text{and} \quad R_{\text{line}} = R_r \times \frac{V_s - V_{\text{line}}}{V_{\text{line}}}$$  \hspace{1cm} (2)

Where the measured voltage ($V_m = V_s - V_{(\text{analyte, line})}$) is taken directly from the signal when it reaches saturation (signal ceiling) as a function of time. We applied this algorithm to all the devices tested in this study. We tested sensors with SnO$_2$-CNT composite as the active material and, for comparison purposes, we also tested sensors with bare CNTs and bare SnO$_2$.

### 4.3. RESULTS AND DISCUSSION

#### 4.3.1. Morphology of the active material

The HRSEM images (Fig. 4) show that the SnO$_2$-CNT composite films consist of randomly oriented carbon nanostructures embedded with SnO$_2$. Each panel inside Figure 4.4 shows different aspects of the nanocomposite: (a) clusters of SnO$_2$ particles
embedded in CNTs, (b) sporadic presence of Cu nanoparticles (~0.3 at wt. % estimated by energy dispersive spectroscopy), (c) SnO$_2$ particles over CNTs, and (d) bamboo-shaped CNTs decorated with SnO$_2$ nanoparticles. The films are uniformly dense over the whole substrate (1.4 cm diameter). The carbon nanostructures mainly consist of bamboo-like carbon nanotubes with diameters between 100 to 200 nm and more than 10 μm of length.

The SnO$_2$ nanoparticles are found randomly distributed over the CNTs surface. They form clusters around 30-100 nm, and they can also be found isolated in sizes around 5-20 nm. Cu nanoparticles can also be found, which come from the substrate. The SnO$_2$-CNT nanocomposite results in a network structure with a very high surface-to-volume ratio. Transmission electron microscopy images (Figure 4.5) confirm that the resulting hybrid material consists of CNTs free of catalytic metallic particles (Figure 4.5a), not covered, but partially decorated with SnO$_2$ nanoparticles (Figure 4.5b and 4.5c). This hybrid structure is a direct consequence of the one step growth process hereby employed, as opposed to sputtering, coating or painting SnO$_2$ onto the CNTs.
**Figure 4.4.** High resolution scanning electron microscope images of: (a) clusters of SnO$_2$ particles embedded in CNTs, (b) SnO$_2$ particles over CNTs, (c) sporadic presence of Cu particles, and (d) bamboo-shaped CNTs decorated with SnO$_2$ nanoparticles.
Figure 4.5. Transmission electron microscopy images of bamboo-like CNTs showing that: (a) they are free of catalytic metallic particles, (b) they are partially decorated with tin dioxide nanoparticles, and (c) close-up view of the tin dioxide nanoparticles on the CNTs.
Figure 4.6. Voltage response of the sensors to alcohol vapors under cyclic exposure to: a) methanol, and b) ethanol.
4.3.2. Performance of SnO$_2$-CNT nanocomposite in detecting alcohol vapors

The response of SnO$_2$-CNT nanocomposite to methanol and ethanol is shown in Figure 4.6a and 4.6b, respectively. They show the behavior of the voltage signal (response) as a function of the time, while the active sensor materials were exposed to different alcohol concentrations at room temperature. The individual response of SnO$_2$ and CNTs is also shown for comparison. Notice that SnO$_2$ alone essentially shows no response, whereas CNTs show a significant response to both types of alcohols. Nonetheless, the integration of SnO$_2$ into CNTs enhances their response by 1.8 and 2.4 times, for methanol and ethanol, respectively. Moreover, the SnO$_2$-CNT nanocomposite keeps the good repeatability and reversibility of the host CNT material. We observe that while the analyte is released into the test chamber (gas ON), the response time is around 45±5 seconds. Analogously, when the analyte is removed from the test chamber (gas OFF), the response decreases quickly with a recovery time of 35±5 seconds. The response time and recovery time are defined here as the time required for the signal (voltage) to reach 90% of the total signal, or decay the total signal by 90%, respectively.

Figure 4.7 shows the alcohol sensitivity values of SnO$_2$-CNT, CNT and SnO$_2$ obtained from Equation 1. The plots indicate that there is a linear relation between the relative resistance ($\Delta R$) and the alcohol vapors concentration ($\Delta C$). The sensitivity values obtained with methanol (Figure 4.7a) are $13 \times 10^{-2}$, $7.55 \times 10^{-2}$, and $1 \times 10^{-2}$, for SnO$_2$-CNT, CNT and SnO$_2$, respectively. Similarly, the sensitivity values obtained for ethanol (Figure 4.7b) are $15 \times 10^{-2}$, $6 \times 10^{-2}$, and $1 \times 10^{-2}$, respectively. In both cases, the sensitivity of the nanocomposite material is somewhat improved in comparison to CNTs.
The correlation coefficient is $0.94 \pm 0.03$ for all the curve fits of MeOH and EtOH in Figure 4.7.
The performance of carbon nanomaterials in the gas detection process has been explained in various studies. Varghese et al. [34], for example, reported that the carbon nanotubes undergo reversible adsorption. During gas exposure, two kinds of adsorption can take place: molecule-CNT interaction via intermolecular forces, and charge transfer through valence forces inducing a change in the CNTS surface conductance (undoped, n-type or p-type, since both materials share a similar work function) [35, 36]. Other studies [18, 37] show, from an experimental point of view, that mixing CNTs into SnO$_2$ has great influence on its detection performance depending the amount and diameter of the CNTs. Large amounts of multi-walled carbon nanotubes (MWCNTs >15%) mixed with SnO$_2$ change the linear relation between the response and the analyte gas concentration decreasing the performance of the material. Moreover, Van Hieu et al. [25] found that CNTs of diameters below 10 nm produce lower responses than those of 100 nm and explained that this effect may be strongly related to the size of the gas molecule adsorbed on the material.

4.3.3. Response of SnO$_2$/CNT to H$_2$S

SnO$_2$ is well known to have limited sensitivity to toxic gases at room temperature [28], but we have also seen that the SnO$_2$-CNT nanocomposite has an enhanced response compared to SnO$_2$ alone. Accordingly, the SnO$_2$-CNT nanocomposite was tested for the detection of toxic gas H$_2$S in this work.
Figure 4.8 shows that the sensitivity of the nanocomposite to H$_2$S is of $1.5 \times 10^{-2}$ from ~9 ppm to 200 ppm. The correlation coefficient is 0.81 for H$_2$S in Figure 4.8, which is lower than that of MeOH and EtOH. This may be due to the fact that H$_2$S is weakly polar and the interaction with the sensor material is hence relatively weak. These results corroborate and extend those of Dai et al.[38], who found good sensitivity to H$_2$S at room temperature, but for concentrations above 20 ppm. The mechanism that they proposed is also applicable for the RT sensor hereby described. They explained that H$_2$S is a
reductant gas, losing electrons that are accepted by SnO$_2$-CNT nanocomposite (n-p heterojunction), which compensate free holes thus causing a resistance decrease. Although some role might also be assigned to the Cu present in the hybrid sensor material (~0.3 at wt.% Cu) due to surface electronic states, such Cu effect would require high temperatures, as discussed for the case of H$_2$ by A. Galdikas et al [39]. In our case the measurements are done at RT, thus we assume that Cu has a negligible role in the sensitivity. The heterojunction sensing mechanism of the hybrid SnO$_2$-CNT nanocomposite thus appears to be much more effective than the chemisorption mechanism of SnO$_2$ and the adsorption mechanism of CNTs alone.

The enhanced sensitivity of SnO$_2$-CNT nanocomposite to hydrogen sulfide hereby shown enables its use to monitor the compliance with the recommendations of the National Institute for Occupational Safety and Health (NIOSH) and the exposure limits established by the Occupational Safety and Health Administration (OSHA). NIOSH recommends 10 ppm (15 mg/m$^3$) for 10 minutes as exposure limit, while OSHA established 20 ppm as the permissible exposure limit and 50 ppm for 10 minutes as maximum peak.

Table 4.1 shows the evolution of the development of gas sensors based on SnO$_2$ mixed with CNTs from 2003 until this piece of research. Collectively, the reports quoted in the table confirm that the combination of CNTs and SnO$_2$ significantly improves the sensor response to alcohols and hydrogen sulfide. Notice that most previous reports specify the application of heat to the sensors as a requirement for operation. The temperatures required varied between 30 and 400 °C. Unlike those sensors, the gas sensors hereby described operate at room temperature, thereby reducing the operating costs and hardware bulk, while improving the device reliability through the simplification of the
operating requirements. In general, a trade-off is observed between operating temperature and sensitivity, for those authors who reported the sensitivity values. However, as long as the target detection limit is ≥ 30 ppm for alcohols and ≥ 10 ppm for hydrogen sulfide, the room-temperature gas sensor based on SnO$_2$-CNT composite films represent an advantage over previously reported sensors.

Table 4.1. Summary of the evolution of the development of gas sensors based on SnO$_2$ mixed with CNTs. (N/R = No report, R-T= Room Temperature)

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Analyte</th>
<th>Low detection limit</th>
<th>Response time</th>
<th>Recovery time</th>
<th>Operating temperature</th>
<th>Sensitivity S=ΔR/ΔC</th>
</tr>
</thead>
<tbody>
<tr>
<td>[13] $^{(2005)}$</td>
<td>H$_2$S</td>
<td>50 ppm</td>
<td>~5 min</td>
<td>~1 min</td>
<td>~140-260°C</td>
<td>N/R</td>
</tr>
<tr>
<td>[40] $^{(2005)}$</td>
<td>C$_2$H$_5$OH</td>
<td>10 ppm</td>
<td>N/R</td>
<td>N/R</td>
<td>355°C</td>
<td>&lt;4</td>
</tr>
<tr>
<td>[30] $^{(2006)}$</td>
<td>C$_2$H$_5$OH</td>
<td>10 ppm</td>
<td>~1 s</td>
<td>~10 s</td>
<td>300°C</td>
<td>&lt;10</td>
</tr>
<tr>
<td>[41] $^{(2008)}$</td>
<td>C$_2$H$_5$OH</td>
<td>100 ppm</td>
<td>&lt;10 s</td>
<td>&lt;10 s</td>
<td>210-400°C</td>
<td>&lt;2</td>
</tr>
<tr>
<td>[42] $^{(2010)}$</td>
<td>C$_2$H$_5$OH</td>
<td>250 ppm</td>
<td>~100 s</td>
<td>N/R</td>
<td>190°C</td>
<td>1.58×10$^{-2}$</td>
</tr>
<tr>
<td>[18] $^{(2010)}$</td>
<td>CH$_3$OH</td>
<td>100 ppm</td>
<td>N/R</td>
<td>N/R</td>
<td>200°C</td>
<td>N/R</td>
</tr>
<tr>
<td>[18] $^{(2010)}$</td>
<td>C$_2$H$_5$OH</td>
<td>100 ppm</td>
<td>N/R</td>
<td>N/R</td>
<td>300°C</td>
<td>N/R</td>
</tr>
<tr>
<td>[38] $^{(2011)}$</td>
<td>H$_2$S</td>
<td>~20 ppm</td>
<td>~10 min</td>
<td>~1 min</td>
<td>30-90°C</td>
<td>N/R</td>
</tr>
<tr>
<td>[43] $^{(2012)}$</td>
<td>C$_2$H$_5$OH</td>
<td>100 ppm</td>
<td>N/R</td>
<td>N/R</td>
<td>R-T</td>
<td>4×10$^{-3}$</td>
</tr>
<tr>
<td>This work</td>
<td>CH$_3$OH</td>
<td>30 ppm</td>
<td>&lt;1 min</td>
<td>&lt;1 min</td>
<td>R-T</td>
<td>13×10$^{-2}$</td>
</tr>
<tr>
<td>This work</td>
<td>C$_2$H$_5$OH</td>
<td>30 ppm</td>
<td>&lt;1 min</td>
<td>&lt;1 min</td>
<td>R-T</td>
<td>16×10$^{-2}$</td>
</tr>
<tr>
<td>This work</td>
<td>H$_2$S</td>
<td>~9 ppm</td>
<td>&lt;1 min</td>
<td>&lt;1 min</td>
<td>R-T</td>
<td>1.5×10$^{-2}$</td>
</tr>
</tbody>
</table>
4.4. CONCLUSIONS

We have developed and tested the SnO$_2$–CNTs nanocomposite as the active gas sensor material for devices operating at standard conditions. The SnO$_2$ particles were distributed in the CNTs matrix, as opposed to sputtered, coated or painted onto the substrate. The SnO$_2$-CNTs gas sensor demonstrated a better sensitivity to alcohol vapors and hydrogen sulfide than bare SnO$_2$ or CNTs. Moreover, SnO$_2$–CNTs gas sensors were able to detect alcohol vapors and H$_2$S down to concentrations as low as 30 and 10 ppm, respectively. Hence, the SnO$_2$-CNTs gas sensors are useful for stringent applications, such as road test alcoholimeters and industrial safety.
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Chapter 5

Conformal Coating of Ferroelectric Oxides on Carbon Nanotubes

5.1. Introduction

Bamboo-like CNTs: The multi-functional properties of CNTs make them important materials for nano- and micro-electronics industries. The growth conditions, armchair geometry and chirality determine the shapes, sizes and segmental compartments of CNTs. CNTs can be fabricated in bamboo-like shapes, depending upon the catalyst particle size and upon the ratio of faster CNT growth compared with catalyst movement and bulk diffusion of carbon in the crystal. The periodic structures of different bamboo-like CNT shapes -- rectangular, cubic, quadrilateral, or trapezoid -- is surrounded by graphite sp²-bonded carbon, but along the periphery of these beads, sp³-bonded carbon is supposed to present [1-8]. CNTs have been produced using various techniques, such as electric arc-discharge, laser ablation, pyrolysis and chemical vapor deposition (CVD). Each technique yields different nanostructures and properties of the CNTs, which may be considered as nano-composites, consisting of different components – amorphous and crystalline regions, pores and defects [8-9], which determines how the catalyst particles join the growing structure. Carbon nanotubes have been shown to exhibit superior properties for various potential applications, like electron emitters in flat-panel displays, electrodes in electrochemical sensors, fuel cells, supercapacitors, field effect transistors, scanning probes, etc.
BST is a well-known ferroelectric with high dielectric constants, low loss, and a ferroelectric (FE) to paraelectric (PE) phase transition temperature ($T_m$) near room temperature, $T_m$ also depends upon the fabrication process [10-13]. 3D nanostructures of BST with CNTs significantly enhance the surface area of the nanostructures; this superior surface-to-volume ratio might increase the capacitance of nanostructures. BST itself a good candidate for dynamic random access memory (DRAM) devices and microwave applications; with a suitable [3D] architecture having CNT as inner electrode makes it strong candidate for future high energy density memory elements or high sensitivity sensors applications. Ferroelectrics are widely used as electrical-mechanical energy conversion devices e.g. micro-electromechanical systems (MEMS) for sensors and actuators, which correspond to the five senses and foot & hand of human being [14].

Since Carbon nanotubes are the one of the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. Combination of these two may provide a new class of MEMS based sensors.

There are few reports on the ferroelectric coating on CNT by chemical solution technique; however these ferroelectric-CNTs are not conformally coated [14-17]. Bedekar et al. synthesized the BaTiO$_3$ coating on CNT by chemical solution techniques, still the adhesiveness and conformality of BT is unlikely [17]. There are no reports till now on conformal coating of ferroelectric on BCNT by PLD technique at elevated temperature with required oxygen partial pressure.

Here we report the controlled growth of BCNT by HF-CVD and uniform coating of BST on BCNT thin films by pulsed laser deposition (PLD) at high temperature. Successful conformal coating of functional oxides on BCNT with maize-like BST nano-beads
attached to the outer surfaces is demonstrated. These structures are characterized by FE-SEM, TEM, and Raman techniques.

5.2. Experimental details

Bamboo-like carbon nanotubes (BCNTs) were synthesized using a hot-filament chemical vapor deposition (HF-CVD) process which intertwined across the surface of a copper substrate. This method is known to create thermal conditions for broken molecular bounds in the precursor gas [18-21]. These films were grown on polished copper (Cu) disks of 1.4 cm diameter. After normal hand polishing, we employed fine and ultrafine sandpaper, finally polishing with diamond fine powder of 0.1 μm grain size. Substrates were cleaned in ethanol for 15 minutes in ultrasound. A gas mixture of 2% CH₄:H₂, was used as the carbon precursor gas, and H₂S was used in the amount of 500 ppm (H₂S:H₂). The substrate temperature was kept at 740 °C. The gases with a total flow was of 100 sccm were directed through a rhenium filament heated to a temperature of ~2500 °C. The filament was kept at a constant distance of 8 mm from the substrate. The pressure in the HF-CVD chamber was kept at 20 Torr, and the deposition time was 10 min.

The characterization of BCNTs was studied by scanning electron microscopy (SEM) using a JEOL Model 35 CF and JEOL JSM-7500F field-emission system. Raman spectroscopy of the BCNTs was obtained using a Jobin-Yvon T64000 spectrometer with argon-ion excitation (514.5 nm) at a power density of 0.5 kWcm⁻². Also a Carl Zeiss TEM LEO 922 transmission electron microscope (TEM) operated at 200 kV was used to observe the morphology and nanostructure.
The PLD target: Ferroelectric Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST) powder was prepared by a solid state reaction route. The starting raw chemicals were BaTiO$_3$, TiO$_2$ and SrO powders. The powders were mixed stoichiometrically in methanol and milled with a high energy ball milling for 16h. The mixture is dried in an oven to 50°C and ground again in a mortar for several minutes to break up some agglomerates. The dried powder was then calcined at 1350°C for 15h. The calcined product was ball-milled again for 5h and crushed to fine powder, and a small amount of polyvinyl alcohol (PVA) was added. The powder was then pressed uniaxially into a target of 6 mm thickness and 25 mm diameter at an isostatic pressure of 8 tons. The target was sintered at a temperature of 1350°C. The firing of the disc was performed in a covered crucible with alumina powder.

PLD deposition: Then the BST target was used to deposit on a BCNT/Cu substrate by pulsed laser deposition (PLD) using a KrF excimer laser (Lambda Physik COMPex 205i, $\lambda=248$ nm). The pressure value in the deposition chamber was lowered to $10^{-6}$ Torr before starting the ablation process. The BCNT/Cu substrate was placed in front of the BST target at a distance of 4.5 cm; 300-nm thin films (5000 pulses) were deposited at 10 Hz and laser energy of 250 mJ. The growth was done at an oxygen pressure of 80m Torr at 650°C. The structural analysis was carried out by SEM, TEM and electron energy loss spectroscopy (EELS).
Figure 5.1. Micrograph from HR-SEM of BCNTs: a) before (100 nm inside scale) BST growth; b) and c) after deposition of BST material (100 nm and 10 nm respectively, inside scale).
5.3. Results and Discussion

Uniform BCNTs nanostructures of 70-100 nm diameters were grown by HFCVD on the copper substrate, as can be seen in Fig. 5.1 (a). The growth of bamboo-like fibers is via the tip growth mode. Lin et al. [21] had used a catalyst for the growth of BCNT, on contrast to our process where no catalyst has been used; hence our structures are cleaner. The outer rims of the BCNTs have sp² carbon form. Coaxial cylinders of rolled graphite sheets with uniform diameter and micrometer length can be seen in the SEM micrographs.

Figure 5.1 (b) shows the maize-bead-like form of BST that conformally coated the BCNT nanotubes. These nanotubes were expected to exhibit conformal coating due to formation of BST-based plasma by PLD. This plasma in vapor form attached to the outer surface of the BCNT nanotubes. Small BST crystals of dimension 5 to 10 nm were attached to the BST/BCNT structures (Fig. 5.1 (c)) along their length. The surface of BST favors the formation of nano-crystals in the later stage of deposition. BCNTs and BST-BCNTs were entangled with each other during the growth process and covered throughout their surfaces. Above a critical film thickness BST favors the nanoparticle bead structure; these maize-beads structure are probably due to island growth based on the Stranski-Krastanov growth mechanism [22-23].

BCNT and BST-BCNT nanotubes grown on Cu substrate were immersed in 10 ml of isopropanol for ultrasonic treatment. Several drops of ultrasonicated samples in suspension were placed on a copper grid for TEM examination. The TEM characterization was conducted to corroborate the bamboo-like structure before and after
deposition of BST material. Figure 5.2 (a) shows the characteristic quality of bamboo-like
CNT with empty internal regions; these bamboo beads similar to nano-cavities were well connected to each other. These nano-cavities are surrounded by closed walls consisting of a number of graphene layers (Figure 5.2(b)). TEM micrographs revealed that these bamboo-like structures have a diameter around 30–60 nm and lengths longer than a micron. Figure 5.2 (c) allows us to see the details about the shape adopted by BST-BCNT hybrid structures after deposition. Higher magnification TEM images are shown in Figs. 3 (a) and (b). It can be easily seen from the micrographs that the maize-like BST crystals were attached to the outer surface of coated nanotubes. Apart from attached BST crystals; there are several crystals separate from the nanostructures but connected to each other in free space. These nanocrystals may have particular interest and use for sensing applications. The average size of the connecting nano-beads was 15-25 nm with spherical shape; these beads are interconnected with each other. BST films and nano-beads are deposited homogeneously on BCNTs. These BCNT nanotubes or nanobelts are conformally coated with the BST films and above a critical thickness of the oxide films, the small surface area favored oxide nano-beads intertwined with the film surface.

Micro-Raman spectroscopy studies have been performed on the bulk BST, BCNTs, BST-BCNTs and BST-coated BCNT nanorods or ribbons suspended on the Cu-grid for TEM study to check the crystalline quality after high temperature deposition of oxides. Pure BCNT shows two prominent peaks at high frequency around 1355 cm\(^{-1}\) (D band) and 1575 cm\(^{-1}\) (G band) due to the presence of sp\(^2\)-sp\(^3\) carbon structures or nano composites; well defined peaks imply good quality BCNT.
Figure 5.3. Image from TEM shows details of BST/BCNTs nono-tubes and nano-belts surrounded by tinny maize-like BST nano particles.
Figure 5.4. Room-temperature Raman spectra of BST, BST/BCNT/Cu, and BST/BCNT on Cu grids; low-frequency modes are well defined in the first two configurations, whereas high-frequency BCNT modes are predominant in the last and on pure BCNT structures.
Amorphous carbon was detected by Raman spectroscopy not only locally but globally, since the BCNT contains a high density of carbon prior to BST deposition. The Raman spectra of the samples for different geometries are shown in Fig. 5.4. The basic matrix of BST is BaTiO₃, and the sequences of the phase transitions for BaTiO₃ are: cubic (m3m) to tetragonal (4mm) to orthorhombic (mm2) to rhombohedral [22, 23]. Bulk BST at room temperature is pseudo-cubic. Theoretically one should not get any Raman-active modes at room temperature, since all ions lie at inversion centers and all long-wavelength optical phonons have odd parity; however, broken symmetry at the nanoscale allows these modes to become Raman-active. This phenomenon is well established for disordered relaxor ferroelectric materials. BST also exhibits compositional disorder at the nanoscale, hence frequency dependent relaxor dielectric properties. Our crystals showed Fm3m face-centered cubic structure above and below their phase transitions also showed Raman active modes, with intensities dependent upon the growth techniques and conditions [23]. Bulk BST crystals show five Raman-active modes at 270, 305, 510, 570, 720 cm⁻¹, of which the last two modes are broader and asymmetric (Fig. 5.4). The BST-BCNT hybrid structures also displayed the same Raman-active modes; the low-frequency mode of BST/BCNT coated nanotubes is lower than the bulk BST, suggesting greater stress present in composites. The ferroelectric soft mode is usually very sensitive to strain in thin films and nanostructures. It is well proven experimentally and theoretically that the E(TO) component of the BT or BST perovskite nanostructures is markedly changed from the bulk counterpart and attributed to the effect of internal stress. [22-26]. The frequency shift of lowest E(TO) mode depends on the type of internal strain developed during the growth period or between the substrate and 2D thin films, this effect is prominent below
the critical thickness typically 400 nm of films [26]. Most likely, an upward shift in the frequency was observed for due to the internal in-plane 2D compressive stress caused by the lattice mismatch whereas tensile stress mainly cause downward shift in the frequency. These phenomena are well observed in the BT/ST and BT/BST superlattices grown on the MgO substrate [26].

One should also expect the less ferroelectric phase transition temperatures of these nanostructures compare to bulk counterpart. The dense layer of hybrid structure does not allow the laser to penetrate the composite to give rise to the BCNT Raman signal from BST-BCNT hybrid structure; however we have observed weak broad BCNT Raman modes signals at high frequency (shown in the inset of Fig.5.4). The BST-BCNT nanotubes and ribbons suspended on the Cu grid exhibit highly intense BCNT Raman active modes, at the same time BST modes appear with weak intensity. The analysis of Raman spectra revealed the BCNT structure remained intact after the BST growth.

The phase evolution during the preparation of the Ba$_{70}$Sr$_{30}$TiO$_3$ for make PLD-pellet was studied using X-ray diffraction (XRD), the spectra is in Figure 5.5 (a) which exhibited cubic crystal structure with perovskite phase[27]. The PLD technique was first employed to cover platinized Si with BST and identify the parameters required to form the same crystal structure as the BST target. Figure 5.5 (b) shows the diffractogram of the fine particles (nano-sizes) of BST on CNT that were formed at a temperature in the range of 650°C to 750°C. Unfortunately, the XRD of BST/BCNT does not provide enough information to determine clearly the crystal structure compared from the BST-pellet. The
integration of BST on BCNT was nonetheless corroborated by EELS and EDS. In some other related works [28, 29], they found that a high level of contamination is present in oxides on CNT that produce absorption and/or undesirable XRD signals that interfere with the crystal structure identification.

**Figure 5.5.** a) XRD pattern of Ba$_{70}$Sr$_{30}$TiO$_3$ pellet and substrate. b) XRD pattern of CNT, BST and BST/BCNT comparison.
5.4. CONCLUSIONS

In conclusion, we have successfully grown ferroelectric-on-carbon nanotube BST-BCNT hybrid structures at high temperatures without much deformation of BCNT nanotubes and ribbons. Thin layers of BST functional oxide films and maize-like nano-beads were conformally coated on the BCNT over micron lengths. High-resolution TEM revealed that the average diameter of the coated structures is 150-250 nm with 15-25 nm diameter beads entangled with the structures. Raman spectra taken for the various configurations imply that the both BST and BCNT maintain their structure after the growth. This represents a big step forward from the earlier report [15] of non-functional ferroelectric oxides (lead zirconate titanate PZT) on CNTs. The next step will be to deposit fully registered arrays. This should permit not only prototype devices, but contact with detailed theory for the polarization distribution in ferroelectric nanowire arrays [16].
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Chapter 6

General Conclusions and Recommendations for Future Works

6.1. General Conclusions

In this thesis, it was shown that sulfur-assisted MCD, SMCD and NCD have very promising UV photosensitivity properties. The estimated sensitivity of materials of interest is in the $10^9 \text{sec}^{-1}\text{mV}^{-1}$ range, and time resolution with respect to the UV radiation of such materials is better than 100 ns. For spectral range of $\lambda > 320 \text{nm}$, the tested materials are solar blind. S-assisted MCD, SMCD and NCD can be used for the long time monitoring at the environment and in aerospace applications.

Furthermore, the spectral response of the diamond UV sensors was evaluated in a common configuration (planar) and compared with the photo-response under a configuration based in field emission at low electric field values (0.7V/µm to 1.7V/µm). The measurements used to compare the performance of the UV light on the samples contain marked differences for the NCD and MCD films. The emission is stable and reproducible within different low bias voltage values (20 to 50 volts) allowing the possibility to easily switch currents optically at room temperature. Field emission configuration through the electrons that are photo-induced with UV light is improved by the properties of sulfur-assisted crystalline diamond films and an effective grain size, proving an alternative option for diamond based detectors.
We also developed and tested the SnO$_2$–CNTs nanocomposite as the active gas sensor material for devices operating at standard conditions. The SnO$_2$ particles were distributed in the CNTs matrix, as opposed to sputtered, coated or painted onto the substrate. The SnO$_2$-CNTs gas sensor demonstrated a better sensitivity to alcohol vapors and hydrogen sulfide than bare SnO$_2$ or CNTs. Moreover, SnO$_2$–CNTs gas sensors were able to detect alcohol vapors and H$_2$S down to concentrations as low as 30 and 10 ppm, respectively. Hence, the SnO$_2$-CNTs gas sensors are useful for stringent applications, such as road test alcoholmeters and industrial safety.

We also synthesized ferroelectric-on-carbon nanotube BST-BCNT hybrid structures at high temperatures without much deformation of BCNT nanotubes and ribbons. Thin layers of BST functional oxide films and maize-like nano-beads were conformally coated on the BCNT over micron lengths. High-resolution TEM revealed that the average diameter of the coated structures is 150-250 nm with 15-25 nm diameter beads entangled with the structures. Raman spectra taken for the various configurations imply that the both BST and BCNT maintain their structure after the growth. This represents a big step forward from the earlier report of non-functional ferroelectric oxides (lead zirconate titanate PZT) on CNTs.

**6.2. Recommendations**

During diamond synthesis, amorphous carbon in different amounts covers the sample film at the end of the process, this is undesirable. As recommended, keep the samples in hydrogen during several minutes while filament-ON, this procedure helps to clean the
diamond surfaces films and enhance the H-terminations, ideal for the photosensitivity transduction.

The presence of H$_2$S (500ppm) and high substrate temperature reduces the diamond growth rate and for low substrate temperatures the diamond growth rate increases. Therefore, the addition of H$_2$S as a sulfur precursor produces a variation in the growth rate and different grain size.

Regarding the uniformity and reproducibility of the samples, after the synthesis these aspects are reflected in statistical-based characterizations, such as TEM examination, in which normally the sample (e.g. nanotubes) on grid are more or less than 1% of the total amount obtained in the experiment. Under this condition, to get some criteria about concepts such as structure uniformity, we need to invest time analyzing different parts of the samples grown. This practice should help to define or fix values in parameters applied in the experiment.

The carbon-based devices here mentioned, gas sensors and the optical detectors, are still as prototypes, due to the detections limits that still remain in laboratory conditions. Fabrication is one of the main challenges needed to find cost-effective, scalable production methods that retain the essential properties of such materials. Therefore, hot filament chemical vapor deposition is the convenient growth method of choice for high-purity CNTs as carbon-based sensitive materials.
Functionalization of the carbon nanomaterial surface (e.g. decorating with metal or metal oxide nanoparticles or by grafting functional groups) is a practical way to increase sensitivity, minimize unwanted effects (e.g., moisture interference) and tune selectivity.

Stability is the main quality indicator in the development of gas sensors for promising real applications. If the material in assessment gives a different sensor response for the same analyte exposed during different times, it is necessary to consider a number of possible reasons:

- Synthesis defects such as grain growth, film cracking, and structural considerations.
- Detection mechanism such as bulk diffusion.
- Errors in measurement design.
- Environmental disturbances such as humidity changes, fluctuations of temperature or electrostatic particles.
- Variations of flow rate.

And possibly more factors affect the sensitivity of the sensor, including the operation of the experimental and data acquisition systems.

### 6.3. Future Works

Through the research work undertaken for this thesis, we have developed a CVD technique suitable for the large-scale synthesis of transparent graphene-based electronic devices. This is a critical step forward in the efforts to develop modern multifunctional portable devices. Therefore, building on the accomplishments described in this research thesis, next generation optically clear electronic components can be developed.