

Development of nitric oxide sensor for asthma attack prevention

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Abstract

The aim of this work is the development of a NO sensor for asthma control and medication monitoring. The transducer is a Molecular Controlled Semiconductor Resistor (MOC SER), which is a GaAs based heterostructure. Protoporphyrins IX, containing carboxylic groups to chemisorb on GaAs, were used as sensing molecules. Characterization of the protoporphyrin monolayers was held using Attenuated Total Reflection in Multiple Internal Reflection (ATR/MIR), High Resolution Electron Energy Loss Spectroscopy (HREELS) in the vibrational and electronic domain and X-ray Photoelectron Spectroscopy (XPS). Degreasing and etching of the GaAs substrates were accomplished before adsorption. Interfacial bonding investigated by ATR/MIR shows that protoporphyrin adsorbs to the GaAs (100) through a unidentate complex and remains mostly vertically oriented. The electronic domain of the HREELS spectra exhibits the Q band with α and β components on the same position as in the UV/Vis spectrum. Soret band is blue shifted showing a face to face stacking of the protoporphyrin molecules on the GaAs substrates. XPS spectra reveal the presence of Cobalt in monolayers prepared with 8×10^{-5} M CoPP solutions. Kinetics is best fitted by an Elovich equation, showing some hindrance due to the previous adsorbed molecules. Thickness found from XPS data ranges from 1.3 to 1.5 nm, which fits with the molecular dimensions. Using the GaAs preparation methods developed here, an NO sensor prototype was assembled and tested for NO sensitivity and repeatability. Relative to NO, tests reveal a good sensitivity between 1.6 and 200 ppb. NO sensitivity was also measured towards CO, CO₂ and O₂. Pure nitrogen sweeps NO from the porphyrin layer, opening the possibility of the sensor reutilization.

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1. Introduction

The past decade has seen an explosion of studies related to nitric oxide (NO). Previously seen as a pollutant and graded as a Class A poison, it was realised that a mechanism existed for “in vivo” synthesis of NO. The discovery of biological functions related to NO arose from conjectures of Robert Furchgott in 1980 regarding a circulating signalling molecule, which he called endothelium-derived relaxation factor that caused vascular smooth muscle to relax [1]. Subsequent to Ferid Murad’s discovery that a gas was capable of regulating important cellular functions, Louis Ignarro confirmed that

Furchgott’s endothelium-derived relaxation factor was, in fact, nitric monoxide NO. The biology of NO advanced rapidly to a point where, in 1992, NO was named “Molecule of the Year” by Science magazine [2]. The 1998 Nobel Prize in Physiology or Medicine was awarded to Robert Furchgott, Louis Ignarro and Ferid Murad for their outstanding discoveries concerning NO as a signalling molecule in the cardiovascular system [3]. It is well-known today that NO acts in the human body as a signalling molecule of key importance in the nervous system as a weapon against infections, as a regulator of blood pressure and as a gatekeeper of blood flow to different organs. It is also established that NO concentration in the exhaled air increases in inflammatory conditions of the airways. In particular, in asthmatic patients it was shown that NO concentration is proportional to the degree of infection: in the exhaled air one could measure 70–80 ppb for sick people and around 10 for

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healthy people [4]. The study here presented is related to the development of a specific pocket sensor to detect the imminence of an asthma attack and to dose the medication in function of the needs. This sensor should be sensitive, NO selective, reusable, low-cost maintenance and cheap.

The construction of this sensor is based on a new device, the Molecular Controlled Semiconductor Resistor (MOC-SER), a GaAs based resistor [5]. The carrier current is controlled by the recognition of the NO by a molecular layer. Due to the high carrier mobility, gallium arsenide (GaAs) is obviously a promising material for building fast response electronic devices for chemical sensing. MOCSEs can be used as a new type of sensor, when coated with specially synthesized bifunctional organic molecules chemically bound to the surface of the device and containing molecular recognition functions. For this purpose, a GaAs based heterostructure is modified, in a way that carriers are confined in a depth less than 50 nm from the surface to improve the sensitivity of the device. The interaction of the recognising molecules with the analyte varies the carrier current in the semiconductor. Any change in the charge distribution in the vicinity of the surface, as for instance the interaction of NO with porphyrin, implies a variation on the carrier current. Also, the thickness of the oxide layer as well as eventual contaminations must be reduced. Several wet-etching procedures were compared leading to a HF etching procedure selected as the most efficient method of the surface preparation [6].

As functional materials, porphyrin and its derivatives exhibit remarkable properties for applications in different fields such as oxygen storage, electron transfer, redox catalysis and gas sensing devices [7]. Two molecules were used in this study: the ferriprotoporphyrin IX chloride (hemin) and the cobaltic protoporphyrin IX chloride (CoPP). Protoporphyrins IX have three kinds of substituents: two lateral propionic groups, two vinyl groups and four methyl groups. The acidic groups enable their chemical adsorption on the residual oxide layer remaining after etching on the GaAs (100) surfaces.

The nature of the interfacial bonds as well as the fractional coverage of the porphyrin layer, crucial to stabilize the GaAs surface and to ensure the properties of response of the sensor, was studied. Protoporphyrins also possess side groups namely propionic groups, which can be used to bind the porphyrin to the GaAs substrate. The surface and the interface of the porphyrin layer were analysed using several techniques having different analysis probing depths: of the order of 10 nm for X-ray Photoelectron Spectroscopy (XPS) and 1 nm for High Resolution Electron Energy Loss Spectroscopy (HREELS) in impact regime. The kinetics of adsorption was studied by Fourier Transform Infrared Spectroscopy using Attenuated Total Reflection in Multiple Internal Reflections (ATR/MIR) with 1500 nm of depth analysis.

Characteristic parameters of the chemisorption were analysed. In fact, besides the adsorption time, several other parameters can play an important role in defining the layer adsorption efficiency as for instance the nature of the solvent or

even the fact of stirring or not the solution during adsorption. This will be analysed elsewhere.

2. Experimental

2.1. Materials

GaAs wafers were undoped semi-insulating single crystals with orientation (100). Acetone and ethanol (anhydric and analytical grade) used for degreasing were purchased from SDS and used without further purification. Hydrofluoric acid (40%) puriss. pro-analysis (p.a.) was delivered by Sigma-Aldrich and diluted to 1% with deionized water with a resistivity of 18.2 M Ω cm furnished by a Millipore system. Dimethylformamide (DMF) was a Fluka HPLC grade (less than 0.02% H₂O). Ferric protoporphyrin IX chloride (hemin) and cobalticprotoporphyrin IX chloride (CoPP) were purchased from Sigma Aldrich and used as received. Fourier Transform Infrared transmission spectra of the free molecules of both porphyrins were recorded using KBr pellets.

After degreasing in anhydric acetone and ethanol (5' each), GaAs substrates were etched with a 1% solution of hydrofluoric acid following a procedure described in Ref. [6]. The GaAs substrates, still containing a very thin oxide layer, were then immersed for 18 h in a 1 mM solution of CoPP in DMF. Other samples were prepared with solutions containing slight amounts of water. Adsorption was held with or without stirring always in the dark. After adsorption, samples were rinsed in pure DMF and then in acetonitrile and dried under an argon flux. ATR/MIR samples were all gently sonicated.

2.1.1. ATR/MIR

The GaAs (100) are highly transparent to the infrared radiation in the spectral range 650–4000 cm⁻¹. Major faces of the ATR/MIR elements, 800 nm thick, were cut in 40 × 15 mm rectangles and optically polished in 45° bevelled edges in an isosceles trapezoidal configuration. ATR/MIR spectra were recorded using a FTIRS Magna-IR Nicolet 850 equipped with a MCT detector. Spectral resolution is 4 cm⁻¹. Kinetics experiments were performed using a homemade Teflon liquid cell provided with a hole for the introduction and the extraction of the solution during the analysis. Spectra were automatically recorded overnight at predetermined intervals. Background was recorded immediately after the solution introduction. In ATR/MIR, the transmitted infrared beam is reflected internally in the GaAs element about 50 times providing submonolayer sensitivity. In each total reflection, an evanescent wave probes the layer with a characteristic penetration depth *l* depending on the wavelength and the index of refraction of the molecular layer and the substrate. In our experimental conditions, *l* is roughly 1500 nm [8], much larger than the thickness of a monomolecular layer.

2.1.2. XPS

The XPS spectrometer used is an XSAM800 (KRATOS) operated in Fixed Analyzer Transmission (FAT) mode, with a

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