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Sensors and Actuators B: Chemical

Enhanced magneto-optical SPR platform for amine sensing based on Zn porphyrin dimers

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ARTICLE INFO

Article history: Received 4 October 2012 Received in revised form 13 February 2013 Accepted 14 February 2013 Available online xxx

Keywords: Gas sensor SPR-MOSPR Magneto-optical signal ZnPP porphyrin Langmuir-Schäfer technique

ABSTRACT

Ethane-bridged Zn porphyrins dimers (ZnPP) have been deposited by Langmuir–Schäfer (LS) deposition technique onto proper transducer layers for surface plasmon resonance (SPR) and magneto-optical surface plasmon resonance (MO-SPR) characterization techniques performed in controlled atmosphere. This last tool has emerged as a novel and very performing sensing technique using as transducer layers a combination of noble and magnetic layers deposited onto glass substrates. A magnetic actuation allows recording a magneto optical SPR signal which ensures best gas sensing performances in terms of signal to noise ratio, sensitivity and limit of detection parameters. Primary and secondary amines in vapour phase have been used as sensing analytes and a possible explanation of the mechanism as well as of the dynamics of the interaction with the sensing Zn Porphyrin layers is provided.

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1. Introduction

Solid state chemical sensors are composed of two main elements: the sensing layer interacting directly with the analyte to be detected and the transducer, necessary to convert the presence of molecules in the environment into a detectable signal. On the sensing layer the vapour molecules are either adsorbed or undergo a chemical transformation, via processes producing the variation of a physical quantity, which is measured by a suitable method, usually through the conversion into an electric signal [1,2].

Porphyrin molecules have been exploited as sensor materials for both inorganic and organic vapours [3] since their optical spectra can be modified as a result of the binding interaction between the porphyrin ring and the analyte vapour molecule [4]. Specifically, zinc substituted porphyrins have demonstrated larger responses to a family of alkylamines due to the specific affinity between the zinc atom and the amine moiety [5]. In this work, surface plasmon resonance (SPR) and magneto-optic SPR techniques have been chosen as transducer techniques. Surface plasmon resonance (SPR) technique is extensively used to monitor the binding of biomolecules to the Au or Ag surface, as well as to monitor interactions between a proper sensing layer deposited onto the Au transducer interface and gas molecules analytes [6]. Surface plasmon polaritons (SPPs) are essentially transversal electromagnetic waves bound to a metal–insulator interface (i.e. materials with dielectric constants of opposite signs) that can be excited on thin metal films for example through gratings or prism couplers. When excited, such collective oscillations of conduction electrons create regions of enhanced electromagnetic (EM) fields in the direct proximity of the metal surface that are highly sensitive to the local changes of refractive index occurring at the surface of the thin metal film, which in turn provides a capability for a label-free form of analytical detection.

Various approaches have been proposed to enhance the sensitivity of such technique [7–9]. Among them a magneto-optic SPR sensor (MOSPR), based on the interrelation of magneto-optic effects and SPR [10,11] has been proposed recently [12–14]. This sensor is based on the use as transducer layers of magnetoplasmonic (MP) multilayers of noble and ferromagnetic metals: Au [15] or Ag [16] as well as Co [17] or Fe [18] are the preferred materials. The large enhancement of MO Kerr effects, recorded when the surface plasmon resonance is achieved, strongly depends on the excitation conditions of the SPP and therefore on the refractive index of the

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^{0925-4005/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.snb.2013.02.057

dielectric in contact with the metal layer, thus providing the sensing principle of the MO-SPR device [19].

The aim of this work is to propose a novel combination of Zn porphyrin (ZnPP) dimers and MP multilayers acting as gas sensing layer and transducer multilayer structure sensors, respectively, for amine vapours detection. To this purpose an ethylene-bridged zinc porphyrin dimer has been deposited in thin film form [20] by Langmuir–Schäfer (LS) method and tested as sensing layer in a novel sensing platform based on MOSPR sensor using as transducer a Au/Co/Au multilayer structure.

Herein we demonstrate that quite uniform films are obtained onto the MP transducer interfaces, and they are able to detect quite reversibly different concentrations of aliphatic amine vapours in dry-air as carrier gas, thus confirming the potentiality of the technique as optimal transducer platform for room temperature amine sensing.

In this work, two typical molecules representative of a primary and secondary aliphatic amine family were investigated, namely *n*butylamine and di-butylamine vapours. The effect of structure and steric hindrance of the analyte molecules is investigated and related to the possible interactions occurring at the interface between the organic layer and the analyte vapours.

2. Experimental details

2.1. Preparation of magneto-optical transducing layers

To evaluate the MP properties of Au/Co/Au transducer a set of 15 nm Au/6 nm Co/25 nm Au/multilayers were deposited on Corning glass substrates coated with 2 nm of Cr to improve adherence. The thickness and the position of the Co layer with respect to the external medium were dictated by the need of preventing it from oxidation and getting the most efficient enhancement of the magneto-optical activity when the SPP in excited, while minimizing the loss of sensitivity due to its optical absorption, according to previous theoretical studies [15]. All layers were deposited by dc magnetron sputtering at room temperature in an ultrahigh-vacuum chamber with a base pressure of 10^{-9} mbar. In these conditions all the constituents layers are polycrystalline and the Co layer has in-plane magnetization.

2.2. Deposition of the ethane-bridged zinc porphyrin dimer sensing layer

The compound used as active material is a commercial ethanebridged Zn porphyrin dimers [21] and the Langmuir curve was obtained by means of a NIMA trough apparatus (area of 450 cm²) and by spreading 150 μ l of ZnPP chloroform solution with a concentration of 0.27 mg/ml onto an ultrapure water subphase (from a Milli-Q system, resistivity larger than 18 M Ω cm). The trough temperature was regulated at 293 K. After the chloroform evaporation, the floating film was continuously compressed at the air/water interface at a speed of 5 mm min⁻¹. All chemicals were purchased from Sigma–Aldrich and used without further purification.

Three layers of the ethane-bridged zinc porphryin dimers were deposited.

2.3. Atomic force microscopy (AFM)

The surface topography of the film was investigated by contact mode atomic force microscopy (AFM) using a VEECO EXPLORER system equipped with a Si₃N₄ pyramidal tip with minimum force between the tip and the surface. Typical tip radius of the AFM probe is 20 nm. The spring constant of the cantilevers is about 0.5 N/m with a natural resonance frequency of 125 kHz.



Fig. 1. Experimental setup for SPR and MO-SPR characterization in dry air and controlled atmosphere. The magnetic field vector is represented; it is applied in the plane of the surface and perpendicular to the plane of incidence of light.

2.4. SPR and MOSPR characterization in controlled atmosphere

SPR and MOSPR characterization was performed by using an experimental bench based on prism-coupled Kretschmann configuration as depicted in Fig. 1. Further details on the experimental configuration can be found in Ref. [19].

Au/Co/Au multilayers were used as transducing layers both in a traditional SPR and in the proposed MO-SPR configurations. Briefly, in the second case, the sensor signal is the relative variation in the reflected p-polarized light, defined as:

$$\Delta R = R(+M) - R(-M)$$

where $R(\pm M)$ are the reflectance of the p-polarized light with the sample magnetically saturated along the direction of the applied magnetic field.

The sensing performances of the prepared Zn porphyrin LS thin films deposited onto Au/Co/Au substrates were investigated towards different concentrations of aliphatic amines, namely primary, and secondary amines, *n*-butylamine and dibutylamine vapours. The choice of a family of alkylamines as analyte vapours is due to the high affinity of zinc porphyrins for nitrogen donors and in particular the specific affinity between zinc and the amine moiety [5]. The main factors affecting adsorption of amines onto metal–porphyrin thin layers are essentially: the central metal ion, the molecular size of the amine and the electronegativity of the nitrogen within the adsorbed amine.

The gas sensing measurements were performed in an homemade flow type test. Dry air was used as the carrier and the reference gas went through a desired organic solvent to make an air stream containing the test organic vapour. A desired concentration of organic vapour at low concentration ranges was obtained by diluting the corresponding saturated organic vapour through a suitable change of flow rate. The delivery of these gases was controlled and automated using a program (except 'program' in computers) developed using Labview software.

In each measurement the porphyrin film was exposed to vapour(s) for about 15 min (necessary to reach a steady state for the sensor signal); then, after the measurements it was flushed with a pure dry air flow for about 20 min to restore the initial conditions. All measurements were performed at room temperature in a thermally conditioned laboratory. Next, fixed concentration of vapours was transferred into the sensor test cell realized in the meander pipe as described above.



Fig. 2. Atomic force microscopy image of the bare Au/Co/Au transducing layer (a) and after the LS deposition of the ZnPP thin layer (b) on a region of 5 μ m \times 5 μ m.

3. Results and discussion

3.1. Langmuir-Schäfer films

The isotherm curve surface pressure (Π) vs area per molecule (*A*) was recorded during the motion of the Teflon barriers of the Langmuir equipment and has been reported previously [20]. The Langmuir curve suggests the existence of a pseudo-gaseous phase ($\Pi < 1 \text{ mN/m}$); then the onset of a new phase with a rapid slope variation is recorded.

3.2. AFM characterization

The morphology of the LS thin film of the investigated Zn porphyrin dimer deposited onto the multilayer Au/Co/Au structure is shown in Fig. 2 and differs strongly from the bare MP multilayer structure. In such transducing assembly the Au layer presents, before the deposition of the organic tri-layer, a typical surface with a very flat morphology. The surface of Au covered by the thin LS Zn porphyrin film follows the surface morphology of the Au film surface as well as a uniform coverage of the transducing underlayer with a granular look reflecting that an increase in root mean squared roughness after Zn porphyrin layer deposition, namely from (0.8 ± 0.2) nm to (1.8 ± 0.2) nm is observed across all sample. The change in optical and morphological features of the thin films at the interface Au/air is shown also in the following SPR and MOSPR characterization.

3.3. SPR and MOSPR gas sensing test

The angular dependence of the reflectivity and the magnetooptical ΔR signal for the Au/Co/Au/glass and the investigated ZnPP/Au/Co/Au sample are reported in Fig. 3. As expected, reflectivity curves have a characteristic dip with a minimum corresponding to a maximum coupling of light into surface plasmons at metal/air interface [21]. Also the magneto-optical ΔR signal, is characterized by a sharp resonance like angular behaviour at around 45°, i.e. when the SPP is excited. When the SPP is not excited, both *R* and ΔR are basically constant in the same angular range (data not shown).

If the metal surface is covered by the sensing layer, the incident resonance angle – i.e. where the reflectivity minimum take place – exhibits a shift towards higher angles. This effect can be ascribed to the optical property modifications caused by the deposition process and particularly to the refractive index change that occurs above the gold layer.

Also in the ΔR signal the angular shift can be ascribed to the change of refractive index due to the presence of a thin film at the Au/air interface, since the magneto-optical ΔR signal represents



Fig. 3. (a) SPR and (b) magneto-optical curves reporting the change in optical features of the Au/Co/Au multilayer after deposition of the ZnPP LS thin films in dry air condition.



Fig. 4. Dynamic curves reporting SPR reflectance signal (a) and magneto-optical signal (b) changes upon interaction with different concentrations (71, 95, 680, 1400, 2000, 3400 ppm) of di-butylamine vapours in dry air spaced out by a flux of bare dry air. The increase in the signal to noise ratio in the MO-SPR signal is evident in (b).

the variation of the reflectance values due to the magnetic actuation and therefore being dependent on the same optical features of the MP multilayer.

Dynamic changes of the two transducing signals can be monitored upon changes of the refractive index of the sensing layer as a consequence of a physical or chemical interaction with a gas analyte. The monitoring of the transducing signal during time at a fixed angle of incidence of light was performed in this work (Fig. 4).

Obviously, sensors performances are limited by the noise of the sensors baselines due to the different natures in the MO and Reflectivity measurements, respectively. Noise relative to SPR sensor signal is three order of magnitude higher with respect to the MOSPR signal.

So, the modulated nature of MOSPR technique ensures a sensor signal characterized by a high signal to noise ratio thus allowing resolving small changes of this optical parameter upon interaction of the sensing layer with the analyte gas.

In Fig. 4 dynamic curves of the plasmonic and magnetoplasmonic transducing signal are reported upon exposure of the LS Zn porphyrin films to increasing concentrations of the amine vapours. The stability and reversibility of the signal are evident, both parameters being important for ensuring the good performance of the sensor. First three pulses of Fig. 4a and b show a similar dynamic behaviour. On the contrary, last three pulses of MOSPR signal present a singular dynamical behaviour: a very sharp increase and a further decay can be evidenced. Such behaviour can be ascribable to a fast superficial dynamics due to a strong interaction of the analyte vapours with the sensing layers so that a fast and complete coverage of the surface is achieved in the first minutes of interaction. The high analyte concentration allows an elevate number of vapour molecules to reach and cover the sensing surface in few minutes as well as to penetrate and diffuse into the sensing layer leading to a change in the density. The arrival of further interacting molecules causes a dynamic process leading to remove from the surface all exceeding analyte molecules until a new equilibrium condition is set on. Therefore, reversibility to baseline condition requires more time than expected.

Such behaviour do not find correspondence in the SPR pulses: the lower signal to noise ratio is now responsible of the minor ability to follow the dynamic of the interactions in details. It can be stressed that the ability of the modulated wavevector to follow optical variations at Au/air interface per unit time allows recording a more faithful representation of the dynamics of interaction between the sensing layer and the investigated analyte.

The response time t_{resp} is considered as the time taken for 90% of the total change in sensor signal saturation to occur, while recovery time t_{rec} value is considered as the time required to reduce the signal to 10% [22]. Response and recovery times were calculated by considering sensor responses achieved at low gas concentrations.

The interaction is a dynamical process towards the achievement of an equilibrium stage where the recovering of the surface of sensing layer is obtained with a different kinetics for the two analyte vapours; a faster rate is recorded by the secondary than by the primary amine vapours.

In both SPR and MOSPR transducer platforms, secondary amines present shorter response and recovery times with respect to the primary amines taken at a similar concentrations. This is consistent with a fast superficial dynamics of interaction.

Calibration curves reporting the two sensor responses with respect to increasing concentrations of the analyte vapours are in Fig. 5. Sensor response here is defined as the relative variation S_{gas}/S_{air} between the signal (either SPR and MOSPR) recorded when the test chamber is filled by the analyte vapours at the given concentration and the signal recorded in dry air.

As it can be observed, the sensor response to tested analytes increases as the amine vapour concentration increases. For any specific alkylamine, the vapour pressure is highest for the primary amine than for the secondary amine, therefore the highest concentration is delivered for the first ones [23]. This means that the sensor response should be expected to be higher for primary amines if the concentration were the dominating effect in the interaction process. In fact, exposure to secondary amines induces larger sensor responses compared to primary amines for both transducing platforms. This means that Zn-porphyrin sensing layer responds to the specific nature of secondary amines rather than simply as a result of the high concentration of an amine of any type, independently from the chosen transducer signal. Indeed, in secondary amines, the increasing of the size of an alkyl group with respect to primary amines allows increased electron donation to the nitrogen. Increasing the electron-donating power of an amine increases the possible bond strength with the active site of the porphyrin films. This trend agrees with results reported in literature for related systems both in solution and in solid state [5,24]. In addition, binding of secondary amines by these porphyrins has been reported in literature [5] to results in an asymmetric porphyrin ring distortion, that is more pronounced with respect to primary amines as a result of the presence of two alkyl group rather than the only one present in primary amines. Evidently, doubling the number of carbon chains is a more effective method of increasing electron-donating power and therefore the reactivity of the amine with the metallic porphyrin.

In order to better understand the sensing process, the obtained data were modelled by one of the isotherm models which describe the adsorption/desorption of gas molecules onto a solid surface.

Here, we assume that the sensor signal increase is proportional to the number of adsorbed gas molecules on the Zn porphyrin surface, following the Freundlich adsorption isotherm $\theta = kP^x$ where *P* is the pressure and *k* and *x* are constants [25]. This consideration suggests that gas molecules are weakly chemisorbed by Zn porphyrin molecules and that the activation energy for the adsorption process increases linearly with surface coverage. The weak chemisorption character of the interaction of the analytes with the ZnPP surfaces ensures the reversibility of the sensing mechanism, which is attained faster by the di-butylamine vapours.



Fig. 5. Calibration curves corresponding to the two different sensing platforms towards different concentration of the investigated primary and secondary aliphatic amine vapours.

By considering the plasmonic signal and the related magnetoplasmonic signal directly related to the number of chemisorbed molecules on the active layer and taking into account that the Freundlich isotherm, at equilibrium, establishes that the concentration of molecular units of adsorbed gas is connected to the partial pressure P of the gas by the relation $[gas_{ads}] \propto P_{gas}^n$ with 0 < n < 1, where *P* is in turn proportional to the concentration C_{gas} of the gas in the mixture, we obtain that the dependence of the sensor signal change upon gas concentration is well described by the relation $S \approx C_{gas}^{\alpha}$, where the number α depends on the stoichiometric coefficients of the equilibrium reaction between ZnPP macromolecules and the amine vapours chemisorbed [26]. Thus, as reported in Fig. 6, a linear plot of log(sensor signal variation) vs log(amine vapours concentration) in the low concentration range can be obtained.

Calibration curves demonstrate also a different behaviour in the interaction of di-butylamine vapours with respect to *n*-butylamine vapours because the saturation of the signal is attained at lower analyte concentrations. This can be ascribable to the fact that the di-butylamine molecule has a higher steric hindrance and a higher density with respect to the corresponding primary amine, thus a lower concentration is required in order to have a similar coverage of the sensing surface producing the same change in the

density of the superficial part of the sensing layer. The layer with their pores completely filled with the vapour molecules undergoes a sharp change in the overall refractive index of the film and, in turn, to the corresponding modification in the SPR response. By assuming a similar degree of filling of the pores for the two investigated vapours, it is likely that the magnitude of the change depends on the refraction index of the analytes (higher in secondary than in primary amines). As a consequence of this, a lower limit of detection can be attained towards di-butylamine vapours. Calibration curves allow extracting important information concerning the sensitivity and limit of detection for the investigated sensors (Table 1). Limit of detection values are calculated by LOD = $3\sigma/S$ where σ is the standard deviation of the signal recorded in a time range of 10 min and S is the sensitivity intended as the derivative of the response with respect to measurand and extracted form the linear part of the calibration curves for each of the investigated analytes [27]. A greater improvement in sensitivity values can be recognized when passing from classical SPR configuration to the magneto-optical SPR configuration. Better sensitivity values added to the best signal to noise ratio, as evidenced in the dynamic curves relative to the two platforms, allows getting improved values of the limit of detection. The improvement is of a factor of 3 for n-butylamine vapours and more interestingly is of a factor 12 in



Fig. 6. Logarithmic plot of the sensors response curves versus the concentration of the investigated analytes in order to verify the occurrence of Freundlich isotherm at equilibrium.

Table 1Comparison of gas sensing parameters for the two investigated experimental platforms.			
	Analyte	Sensitivity (ppm ⁻¹)	LOD (ppm)
SPR	n-Butylamine	2.32×10^{-6}	14,200

t_{rec} (min) t_{resp} (min) 10 8 **Di-butylamine** 4.32×10^{-5} 760 3 6 MOSPR n-Butylamine $5.23 imes 10^{-6}$ 5100 12 97 4.31×10^{-4} Di-butylamine 60 7.5 3

di-butylamine vapours, in accordance to the discussion reported above.

4. Conclusions

Ethane-bridged zinc porphyrin dimers have been deposited in thin film form and tested as sensing layer by using SPR and MOSPR platforms using as transducer a Au/Co/Au multilayer structure. Primary and secondary amines vapours were chosen as analyte molecules. The investigated sensing layers responded to the specific nature of secondary amine as a result of the increased electron donating power with respect to primary amines. Higher steric hindrance of secondary amines is responsible of the rapid coverage of the surface even at low analyte concentration. Secondary amines demonstrated also shorter response and recovery times with respect to primary amines, thus revealing a faster surface dynamics. Freundlich isotherm were used to describe the adsorption of analyte molecules onto the Zn porphyrin layer thus revealing the weak chemisorption character of the interaction.

As expected, MOSPR configuration allows recording an higher signal to noise ratio sensorgram. As a consequence, better sensor performances can be achieved both in terms of sensitivity and of limit of detection. The improvement is of a factor 3 for n-butylamine vapours and of a factor 12 in di-butylamine vapours. Further investigation are in progress in order to correlate sensor signal changes to a variations in refractive index of the sensing layer. The contribution of air humidity is also under study in particular for application of this sensing technique in food industry.

Acknowledgements

This work has been funded by the European Commission (NMP3-SL-2008-214107-Nanomagma), and by the Italian Ministry of Education (FIRB project-Nanoplasmag). The Spanish MICINN (projects MAPS MAT2011-29194-C02-01 and Funcoat Consolider CSD2008-00023) and Comunidad de Madrid (projects Nanobiomagnet S2009/MAT - 1726 and Microseres S2009/TIC - 1476) are also acknowledged. E.F.-V. thanks CSIC for his JAE fellowship, and the Phantoms Foundation and the nanoICT Coordination Action for the funding of a short stay in Lecce.

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Biographies

M.G. Manera received her University degree in Physics and PhD degree in "Material and new technologies" from the University of Lecce, Italy in 2003 and 2006. Her research interests lie in the area of optical characterization of organic and inorganic materials for optochemical sensing and biosensing applications exploiting surface Plasmon resonance transduction methodologies. Recently she has been involved also in the study and functional characterization of metal oxide based gas sensors. particularly when exposed to light illumination. Currently she is involved in the functional characterization of magneto-plasmonic materials as novel magnetooptical transducing platforms for improving the gas and bio-sensing performances of standard surface plasmon resonance sensors.

E. Ferreiro-Vila obtained his Physics degree (optoelectronics speciality) by the University of Santiago de Compostela (USC) in 2006. After that, he carried out his PhD thesis in the Instituto de Microelectronica de Madrid (IMM-CSIC) (2007-2012). This thesis deals with metal and metal dielectric magnetoplasmonic (MP) multilayers, which combine noble metals and ferromagnetic ones and exhibit interrelated effects between the excitation of surface plasmon-polaritons (SPPs) and their magnetooptical (MO) activity. Moreover, these MP systems have been used as transducers in gas and biosensing applications during several short stays in the Istituto de Microelettronica e Microsistemi (Lecce, Italy). This PhD thesis was defended at the end of 2012 in the USC. Now, he is starting a postdoc research in the Center for Research in Biological Chemistry and Molecular Materials (CIQUS) in the USC, involved in the study of the thermoelectric properties of heavily doped semiconductor multilayers.

J.M. García-Martín received his PhD from the Universidad Complutense de Madrid, Spain, in 1999, for his work on cobalt nanowires and cobalt-phosphorus microtubes. He then moved to the Laboratoire de Physique des Solides at the Université Paris-Sud, France, with an individual Marie Curie fellowship, where he worked in magnetic force microscopy (MFM) and micromagnetic simulations. He joined the Instituto de Microelectrónica de Madrid in 2003, where he is now a Tenured Researcher of the Spanish Research Council (CSIC) working within the "Magnetic Nanostructures and Magnetoplasmonics" research line. He is an expert in scanning probe microscopy techniques, especially AFM and MFM, and in magnetic characterization and modeling. He has wide experience in sample growth using e-beam deposition and sputtering. He has co-authored 61 articles and one book chapter, with about 1200 citations to his works, and has given eight invited conferences. His h index is 19. His personal ResearcherID page is: http://www.researcherid.com/rid/H-4434-2011.

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