Sensors and Actuators B 179 (2013) 175–186

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Improved gas sensing performances in SPR sensors by transducers activation

M.G. Manera, R. Rella*

Institute for Microelectronics and Microsystems, IMM-CNR, Via Monteroni, 73100 Lecce, Italy

A R T I C L E I N F O

Article history:
Available online 18 October 2012

Keywords:
SPR
Magneto-optical SPR signal
Gas sensor

A B S T R A C T

In this paper, among all transduction methodologies reported in the field of solid state chemical sensors, the attention has been focused onto the optical sensing characterization by using surface plasmon resonance (SPR) technique and its evolution towards active plasmonics. Activation of the transducer by application of an oscillating magnetic field in a transversal configuration is demonstrated to improve the gas sensing performance of classical SPR sensors. To this purpose a new transducer, composed of metallic and magnetic materials and a proper sensing layer have been chosen. TiO_2 sensing layers have been prepared by two different experimental routes and their optical and morphological features investigated and correlated with their sensing performances. A comparison between classical SPR technique and a new sensing probe based onto magneto-plasmonic effect in resonance condition has been reported. Improved gas sensing performance in terms of sensitivity has been demonstrated in the presence of different alcohol vapours concentration mixed in dry air.

1. Introduction

In the last few years, the development of new sensors based on opto-chemical investigation techniques has generated a considerable international interest. The growing attention to those systems is justified by the presence of many possible areas (industrial, environmental, medical) for which these devices have potential applications. Several industries like the automotive or the biomedical one, together with other fields of research linked with the environmental or food monitoring, always have the need of new sensors characterized by higher performances, cheaper price and lower production time. Considering only the sensors based on a chemo-optic signal transduction, various techniques can be used, for instance spectroscopy, interferometry, ellipsometry, or surface plasmon resonance (SPR) [1–4].

The last one mentioned has recently attracted a large interest for its potential applications in the field of thin films optical characterization [5]. The peculiarity of this technique lies primarily in its ability to investigate physical and chemical processes that occur close to the interface between a metal and a dielectric means, detecting even small changes in its optical properties due to changes in environmental conditions [6–11]. The high sensitivity of this method and the ability to easily run real-time analysis, make surface plasmon resonance an interesting transduction mechanism for opto-chemical sensors [12–16].

However, the constant need of better performances, bring scientists to research new possible materials or different experimental setups, in order to further increase the sensitivity of SPR sensors [17–21]. With this aim, in the last few years innovative techniques for surface plasmon resonance modulation have been proposed in order to achieve a great increase of sensing performances [22–25]. The addition of new features on these devices opened a new field of research known as “active plasmonics”. This name is linked to the possible control of surface plasmon properties by an external agent, such as a temperature variation or the electric or magnetic fields application [26].

The activity presented in this work belongs to the mentioned innovative field of research, since it is based on the modulation of SPR properties through the application of an oscillating external magnetic field [27]. The technique is generally referred as magneto-optic surface plasmon resonance (MOSPR).

The new working principle is based on a mutual interaction between surface plasmon resonance and magneto-optic Kerr effect typical of magnetic materials [28–30]. When the SPR conditions are satisfied, it is possible to obtain a high amplification of MO Kerr effect and this phenomenon can be exploited as a new probe for the development of innovative magneto-plasmonic sensing devices [31,32]. This amplification is highly dependent on the plasmon excitation conditions, and thus indirectly linked with the optical properties (refraction index) of the sensing system. The new combination of materials and transductors give us the opportunity to develop a MOSPR gas-sensing device with possible applications in the field of solid state chemical sensors for gas and/or vapours detection and demonstrate the increase in sensitivity with respect to standard SPR sensors.

* Corresponding author.
E-mail address: roberto.rella@cnr.it (R. Rella).

0925-4005/$ – see front matter
http://dx.doi.org/10.1016/j.snb.2012.10.028

To this purpose SPR and MOSPR optical sensing tests have been performed by using as sensing layer TiO_2 thin films deposited by using two different methodologies onto the relative transductors. A comparison of the two transducer platforms is outlined as well as the contribution of the sensing layers features on the gas sensing performances of the proposed sensors.

2. SPR sensors: passive and active configurations

2.1. SPR sensors

Generated by the interaction between the electromagnetic waves of a p-polarized light with the free electrons of a conducting layer, surface plasmon polaritons (SPPs) are collective charge density oscillations localized at the interface between two materials with dielectric constants of opposite sign (metal and dielectric materials). These plasma oscillations are linked with evanescent electromagnetic waves that can propagate only along the interface between the two media.

Optical sensors based on resonant excitation of surface plasma (SP) waves, are optical devices that exploit the sensitivity of the propagation of an SP wave, to measure in real times changes in the refractive index of an active layer [10–16,33,34].

Attenuated total reflection (ATR) in prism couplers, in particular the Kretschmann geometry, has been widely used for the excitation of SP waves in SPR sensors. In this configuration the optical wave is totally reflected at the interface between a prism and a thin metal layer and excites an SP wave at the outer boundary of the metal. The excitation of an SP wave results in a drop in the intensity of the reflected light. This may be observed as a dip in the angular or wavelength spectrum of the reflected light (Fig. 1). All the main detection approaches have been demonstrated in SPR prism-based sensors: intensity modulation [11,12], angular modulation [35,36], wavelength modulation [22], phase [23] and polarization modulations [37]. Prism-based SPR sensors using angular interrogation have been extensively developed into numerous research laboratories and in several commercial SPR instruments [38]. Miniaturized SPR sensors using the ATR method have been developed as an alternative to laboratory SPR systems to allow the development of mobile, compact, and cost-effective sensing devices for field applications [39].

2.1.1. SPR technique for the characterization of thin films

Among all its important characteristics, it can be also recognized that SPR technique is a surface-sensitive spectroscopic technique that can be used to characterize a variety of ultrathin monolayers and multilayers deposited onto gold, silver and copper surfaces. SPR technique is, over other optical techniques, a unique combination of an extremely high sensitivity to optical properties of surface layers and the ease of their real-time continuous monitoring. Any variation in the refractive index at gold surface, i.e. due to the presence of a thin film, will turns in a change in the angle of incidence for the excitation of surface plasmon. For this reason SPR technique represents a valid tool to probe the optical constants (n; k) and thickness (d) of a thin layer deposited onto a thin film metal surface.

Optimization methods are used to solve a set of non-linear equations obtained by the following procedure. Generally, the optimization scheme provides the minimization of suitable objective function. Assuming x to be a set of the model parameters (n, k and d for different layers), the objective function $F(x)$ for minimization can be taken in the form:

$$F(x) = \sum [R_i(x) - R_i^0]^2 \tag{1}$$

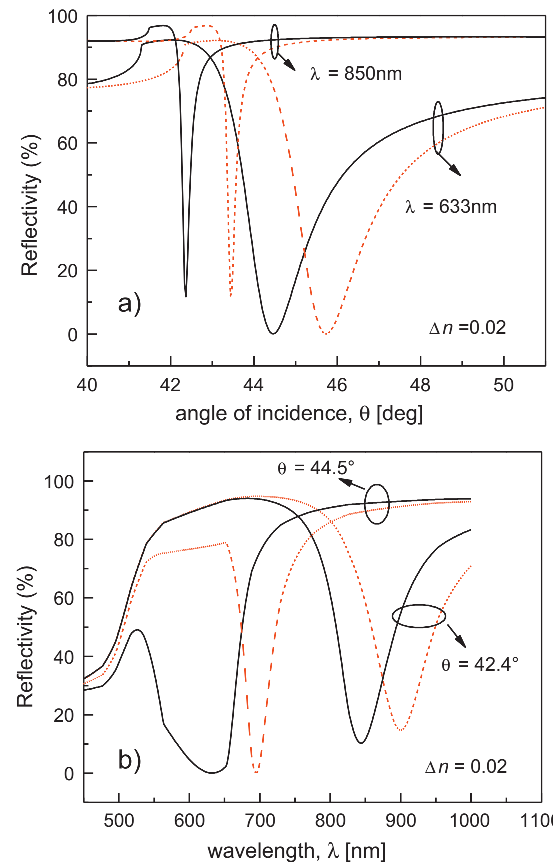

Fig. 1. (a) Reflectivity as a function of the angle of incidence of light and calculated for two different operation wavelengths and two different refractive indices of the analyte. (b) Reflectivity as a function of the wavelength calculated for two different angles of incidence and two different refractive indices of analyte (configuration: BK7 glass prism-gold 52 nm – analyte).

where $R_i(x)$ is the computed reflectance, R_i^0 is the experimental one and the subscript i denotes the data point number. This procedure is applied repeatedly until local minimum of $F(x)$ is reached.

The optical parameters of the *active layer* deposited onto the gold film can be extracted using a suitable model simulating the real structure of the investigated layer. To this purpose, an effective medium approximation (EMA) is often used to properly describe the effective dielectric constant of composite materials especially when one (or two) of the components has a shape distribution. In the case of a two-component material the treatment can be developed as follows. The dielectric response can be described by a *Maxwell–Garnett* effective medium approximation [40] given by the relation:

$$\frac{\varepsilon - \varepsilon_a}{\varepsilon + 2\varepsilon_a} = f_b \frac{\varepsilon_b - \varepsilon_a}{\varepsilon_b + 2\varepsilon_a} \tag{2}$$

where ε_a and ε_b are, respectively, the dielectric function of the two phases a and b, ε is the effective dielectric function of the heterogeneous medium, and f_b is the fraction phase b.

2.2. Active plasmonics: MOSPR sensors

It is well known that the response of a material to the external action of an electromagnetic field is described by the dielectric tensor. The optical properties of any material are described by the diagonal elements of the dielectric tensor. It describes the reflection, transmission, and absorption response of a physical system to an electromagnetic field without any external excitation. On the contrary the magneto-optical (MO) properties are related to the