Chapter 31
Plasmonic and Magneto-Plasmonic Nanostructured Materials for Sensors and Biosensors Application

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Abstract A new Magneto-Optic Surface Plasmon Resonance (MOSPR) gas sensor is presented. This sensor is based on the combination of the magneto-optic effects of magnetic materials and the Surface Plasmon Resonance in metallic layers. Preliminary results proofed the enhancement in sensitivity of the MOSPR sensor with respect to traditional SPR sensor.

31.1 Introduction

Surface plasmon resonance (SPR) is one of the leading optical methods that provides easy, highly reproducible and sensitive assays for gas an bio-sensing. It relies on the changes in refractive index that occur when a target analyte binds to the metal film or nanoparticles. The sensitivity and limits of detection of SPR sensors can show variations depending on the method used to excite surface plasmons (prism coupling, grating coupling, optical fibers etc.).

Recently, it has been proposed in the literature a novel Magneto-Optic Surface Plasmon Resonance (MOSPR) sensor [1] which performances can be greatly enhanced with respect to traditional SPR sensors (an improvement by a

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G. Neri et al. (eds.), *Sensors and Microsystems*,
Lecture Notes in Electrical Engineering 91, DOI: 10.1007/978-94-007-1324-6_31,

factor of 3 in the limit of detection). The novel device is based on the combination of the magneto-optic (MO) effects of the magnetic materials and the surface plasmon resonance. This combination can be achieved by introducing into the sensing transducer layer a magnetic thin film whose magnetization state change direction alternately during the surface plasmon excitation. By this way, a great enhancement of the magneto-optic effects in the p-polarized light is produced when the resonant condition is satisfied. Such enhancement strongly depends on the refractive index of the dielectric medium, allowing its use for optical gas sensing. Small variations of the refractive index will induce large changes in the MO response, allowing to greatly improve the sensitivity of the MOSPR sensor.

In this work, some preliminary results for both the gas sensing and biosensing schemes are shown. As concerns gas sensing, TiO_2 nanocrystals prepared by chemical route [2] have been deposited in thin film form by spin coating onto the gold surface in contact with the medium to be monitored. Their interaction with Volatile Organic Compounds (VOCs) has been monitored both in a standard SPR and in MOSPR configurations in order to compare their sensing performances. For biosensing applications, the response of the MOSPR device for adsorption of Bovine Serum Albumin (BSA) proteins onto the gold surface and its interaction with its specific antibody has been tested. In both cases a smart enhancement in sensitivity of the MOSPR sensor with respect to the SPR sensor can be evidenced.

31.2 Experimental Setup

The experimental set-up of the MOSPR is very similar to that developed for standard SPR sensors, the only difference is the introduction of a magnetic layer and a magnetic actuator to control the magnetization state of the magnetic layer. In a Kretschmann arrangement, the enhancement of the MO Kerr effects in the reflected light can be achieved through the combination of Co/Au multilayers. If the magnetization is in the plane of the magnetic layer and perpendicular to the propagation plane of the light (transversal configuration), the MO effect produces a relative change of the reflectivity of the p-polarized light.

$$\frac{\Delta R}{R} = \frac{R(+M) - R(-M)}{R(0)}$$

Figure 31.1 shows the MO effects of the p-polarized light in the transversal configurations for a system formed by a Co/Au multilayer in a Kretschmann arrangement in which the incident medium is glass and the outer medium is water. The MO effects are very localized and show a very sharp curve. As a consequence, small variations of the refractive index will induce large changes in the MO response (Fig. 31.2).

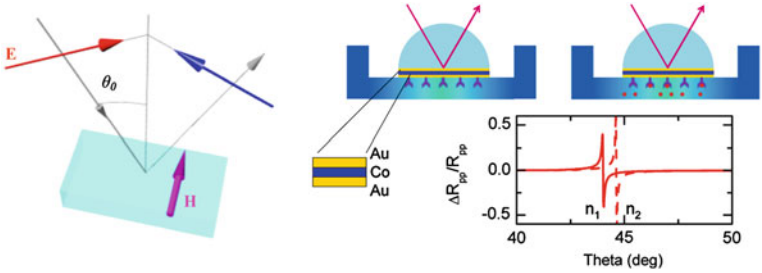

Fig. 31.1 Scheme of the experimental setup for MO-SPR characterization in transversal configuration for gas and biosensing measurements

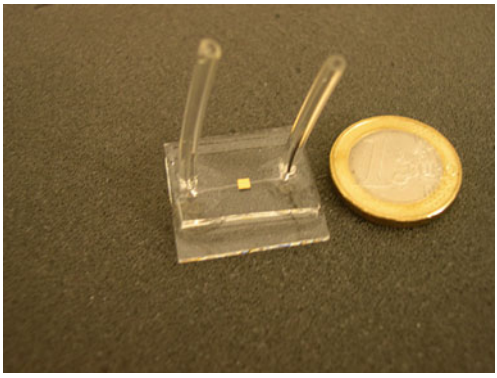

Fig. 31.2 Picture of the sensing chip provided with microfluidics channel for inlet and outlet of analytes

31.3 Preparation of the Sensing and Biosensing *Active Layers*

Au/Co/Au multilayers were deposited by dc magnetron sputtering in an ultra-high-vacuum chamber after a thin layer of Cr adhesion layer onto two different glass slides: BK7 ($n = 1.5$ at $\lambda = 633$ nm) for gas sensing purposes and SF10 ($n = 1.7$ at $\lambda = 633$ nm) for biosensing purposes.

The thickness of the involved multilayers are the following (starting from the glass): 2 nm Cr /25 nmAu/ 6 nm Co/ 15 nm Au. These values have been choosen on the basis of a theoretical simulation of the MO activity of such layers with respect to the sensing application.

In addition, a thin film of TiO_2 nanocrystal were spin coated onto Au/Co/Au multilayers deposited on BK7 glass and used as active layer for gas sensing purposes. Instead, the multilayers deposited onto SF10 glass have been used for biosensing, namely they have been properly functionalized for the further immobilization of BSA proteins.

31.4 Fabrication of Microlfuidics Devices

The inlet and outlet of solutions containing the investigated biomolecules in each step is carried out by microfluidics channels which have been realized on purpose. The fabrication of microfluidics device is based on standard photolithography techniques for master realization.

The SU-8 photoresist is applied n a Silicon wafer with spin-coating process at 500 rpm for 5 s and at 4000 rpm for 40 s, after the master is placed in oven and cured at 65°C for 1 min and at 95°C for 3 min. The exposure to UV radiation is for 80 s followed by another thermal process for 1 min at 65°C and 3 min at 95°C. The hard bake phase is developed at 200°C for 10 min.

The replicas of the inverse pattern is produced using the PDMS of Sylgard; the mixture pre-polymer and current agent is 10:1. The PDMS is cured at 70°C for 1 h or more and peeled off the master, producing the final replica bearing the designed microstructures. Small holes are drilled into the PDMS using a borer to produce inlets and outlets. Finally, PDMS can seal to itself and other flat surfaces reversibly by conformal contact (via van der Waals forces), or irreversibly if both surfaces are Si-based materials and have been oxidized by plasma before contact (a process that forms a covalent O–Si–O bond).

The channel dimensions are 100 μm × 30 μm × 1.5 cm (width, height, length) (Fig. 31.2).

31.5 Results and Discussion

The sensing layer was deposited by spin coating onto the MOSPR substrates (corning glass/Cr/Au/Co/Au); a 35 nm thin layer of TiO_2 nanoparticles prepared by a chemical route was obtained and tested by SPR and MOSPR in controlled atmosphere.

Sensing tests in the presence of mixture of VOCs (ethanol, methanol, isopropanol) sent in the test chamber at different concentration were performed. Preliminary measurements allows obtaining information about the increasing in the sensitivity towards the considered alcohol vapour when a magnetic field is present. Measurements in the presence of different analytes are in progress (Fig. 31.3).

Biosensing tests have been carried out on similar Au/Co/Au multilayers deposited on SF10 glass substrates. First, the investigation was devoted to find the proper conditions of preparation of the multilayers on glass substrates in order to get an high efficiency of immobilization of biomolecules. A morphological characterization of the Au/Co/Au multilayer after the immobilization procedure confirmed the presence of at least one monolayer of proteins onto the Au surface wich results from different features having an higher thickness and less sharp edges.

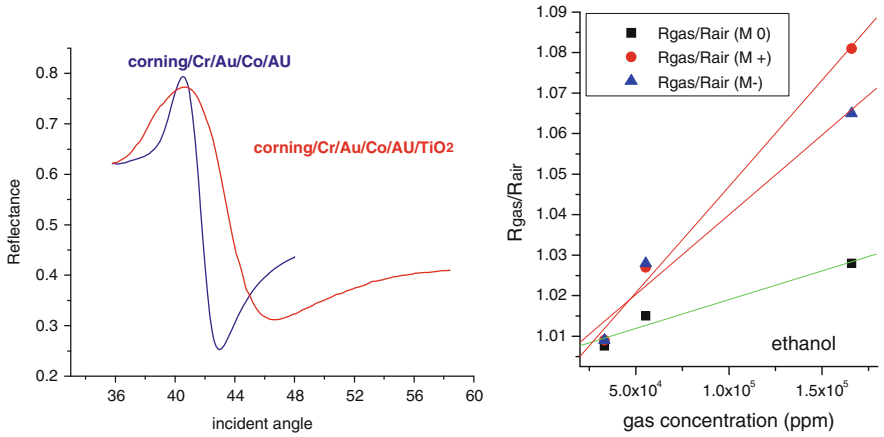

Fig. 31.3 Comparison of SPR curves of the bare Au/Co/Au multilayer on glass and after consideration of TiO2 sensing layer; Sensor calibration comparison relative to ethanol vapours

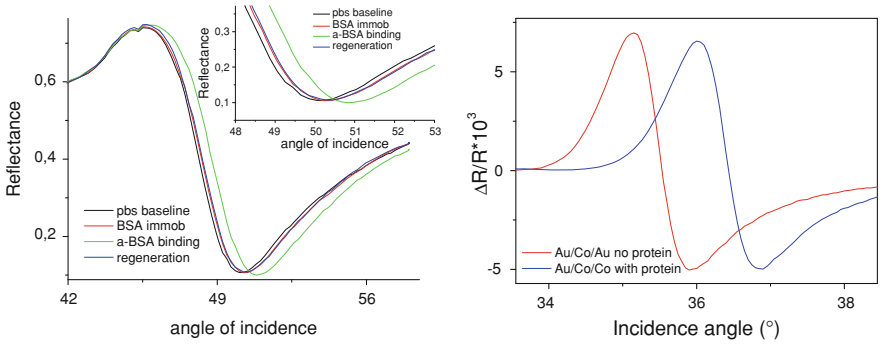

Fig. 31.4 SPR and MOSPR curves comparison relative to each step of the biosensing protocol. The shift in the curve minima upon protein immobilization is apparent

A complete biosensing test has been carried out onto the Au/Co/Au deposited on SF10 glass substrates and each step have been monitored by SPR characterization in liquid conditions.This biosensing tests consisted in the following steps:

- baseline in buffer condition
- immobilization of BSA protein dissolved in the same buffer solution (500 ppm)
- binding between BSA protein and the anti-BSA antibody (300 ppm)
- regeneration step consisting in the separation of anti-BSA antibody from the protein in order to control the ripetibility of the measurement.

Figure 31.4 shows the SPR curves recorded in correspondence of each mentioned step in absence of a magnetic field.

Also in this case, a shift of the minimum of the curve towards higher angles can be noticed, thus confirming the presence of at least a layer of proteins onto the Au surface.

Preliminary measurements of the dynamic interaction BSA protein/anti-BSA performed in liquid phase by SPR equipment give us information about the binding and allows us to compare the results obtained without the application of a magnetic field and after applying a magnetic field in trasversal configuration.

31.6 Conclusions

In this work preliminary results concerning the increase in sensitivity of a MOSPR sensor and biosensor are presented. For gas sensing, a TiO_2 nanocrystal based thin film has been used as active layer, for biosensing the immobilization of BSA protein onto the Au/Co/Au multilayer have been analyzed reporting interesting and promising results that are going to be further investigated.

Acknowledgments This work was supported by Nanomagma Euorpean Project.

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