Optical microsensors for pesticides identification based on porous silicon technology

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Abstract

A simple and low cost optical sensor, based on porous silicon nanotechnology, has been used to detect and quantify the presence of atrazine pesticide in water and humic acid solutions. In both cases, a well defined optical signal variation can be registered, even at low concentration as 1 ppm. The phenomenon can be ascribed to the capillary infiltration of liquid into the pores, which changes the average refractive index of the structure. Due to the resonant cavity enhanced operation of the proposed sensors, very low detection limits can be reached.

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1. Introduction

Pesticides are chemical substances which are used to kill unwanted organisms, so that they are a vital input in today’s agriculture, protecting food and fiber from damage by insects, weeds, diseases, nematodes, and rodents. On the other hand, pesticides often act as nerve poisons and are often hazardous to animals and humans: some can cause nerve or liver damage, birth defects and cancer. In the last few years, new kind of pesticides are progressively replacing organochloride insecticides, fungicides and herbicides like DDT, Lindane and Aldrin, due to their lower environmental persistence. Nevertheless, even these new pesticides are toxic and they can be destructive for the equilibrium of ecosystems. In particular, triazines are herbicides of common application, used in feeding and non-feeding (e.g., pasture) purposes. They can be also employed in other fields, as golf green or parks care. Atrazine (2-chloride–4-ethylamine–6-isopropyl amino–1,3,5-triazine) is a anthropogenic herbicide and it appears as a white solid, colourless, non-volatile, poorly soluble in water, with a cyclic chlorinated structure. Some chlorinated metabolites of Atrazine such as desethylated atrazine (DEA), desisopropyl atrazine (DIA), diaminochlorotriazine (DACT) are also very toxic (Kellog et al., 2000).

The analytical methods, commonly used to detect and quantify the presence of such pollutants in environmental matrices, are complex and time consuming: many samples must be collected, and then the organic fraction is separated from the rest of the mixture, i.e., by using HPLC; after that, a purification step is needed and substances have to be identified. This last action may require techniques such as NIC-GCMS, and GC/FT-IR, in order to reach an univocal information on compounds structure (Culea et al., 1996; Nakagawa et al., 2001). The overall analytical process is complex, expensive, and relies on skilful manpower. To overcome these difficulties, lot of biosensors for the determination of organophosphorus pesticides have been proposed in literature (Roger...
Its high surface area, on the order of 500 m$^2$/cm$^3$, assures that porous silicon (PSi) is very interesting for its peculiar physical properties. Among usual materials for optic applications, porous silicon structures are: pore diameters in the range of 3–100 nm, porosities of 10–90%. Both properties are dependent on the etching current density, producing high refractive index layers, is 250 mA/cm$^2$, which corresponds to a porosity of 69%. It is applied for a time of 0.634 s in order to obtain a porosity layer of 95%.

The optical sensors have a microcavity structure made of two distributed Bragg reflectors (DBRs) with a Fabry–Perot film of λ/2-thickness in the middle. Several alternating pairs of PSi-layers, having different refractive indices, obtained modulating their porosity, constitute the DBRs (see Fig. 1). The optical thickness (nd) of each single-layer in the DBRs is λ/4, where d is the physical thickness of the layer, n its refractive index and λ is the Bragg wavelength. The whole stack is an optical resonating structure at the Bragg wavelength, whose characteristic is that of a high reflectivity pass band filter with a narrow transmittance peak approximately in the band centre. The band shape and the peak width are controlled by a proper design of the layer stack. In our experiments, we used a PSMC produced by electrochemical etching on p-type (ρ = 10 mΩ cm) standard silicon wafer. The DBRs, over and under the optical cavity, were constituted by seven periods of alternated high and low refractive index layers. The Fabry–Perot cavity is a double-thickness, high porosity layer. The etching current density, producing high refractive index layers, is 250 mA/cm$^2$, which corresponds to a porosity of 69%. It is applied for a time of 0.634 s in order to obtain the required thickness of 212 nm. Low refractive index layers require a current density of 550 mA/cm$^2$ for 0.55 s, leading to a porosity of 89% and thickness of 288 nm. This optical structure has one single resonance peak in the reflectivity pass band around 1350 nm, as shown in Fig. 2.

For quantitative determinations, we have prepared two sets of atrazine solutions in a range of concentration between 1 and 50 ppm: (1) atrazine in pure water, (2) atrazine in an aqueous solution of a humic acid (HA, 0.2 mg/ml) extracted and purified from a North Dakota Lignite (Piccolo et al., 1998). All solutions were obtained by dilution from a 50 ppm solution of atrazine in ultrapure water, obtained by stirring 5 mg
Fig. 2. Reflectivity spectrum of a PSi optical microcavity.

The optical setup required for our sensing experiments was simple: a tungsten lamp (white source, 400 < \( \lambda \) < 1800 nm) inquired, through an optical fiber and a collimator, the sensor at nearly normal incidence. The reflected beam was then collected by an objective, coupled into a multimode fiber, and then directed into an optical spectrum analyzer (Ando, Japan). In this way, we measured the reflectivity spectra over the 1100–1600 nm range with a resolution of 0.2 nm.

The sensor active surface was a circle of about 1.5 cm diameter and the light spot was only 3.4 mm, so that the transducer dimensions could be really miniaturised.

Measurements started after drying the sensor with a soft nitrogen stream; then a small drop (about 10\( \mu \)l) of solution containing atrazine, either aqueous or humic, was placed on the surface of the sensor and covered with a thin transparent glass.

Each experimental point was the average on five independent measurements, the error bar representing the standard deviation. Independent acquisitions, which increase the precision of the results, were obtained by exposing the PSi chip to the same amount of solution.

4. Results and discussion

When the PSMC is wetted by liquid substances or water solutions, a repeatable and completely reversible change in the cavity reflectivity spectrum was observed. We assume that the partial substitution of air by liquid in the pores of each layer determines an increase of the average refractive index of the microcavity. In fact, in case of pure water, \( n = 1.3300 \) at \( \lambda = 589.3 \) nm (Na yellow spectral line) and \( T = 25^\circ C \), this results in a marked red-shift of the cavity characteristic peak.

The red-shift of the resonant cavity peak was characteristic of each concentration and the phenomenon was completely reversible and reproducible. Experimental results for both sets of solutions are reported in Fig. 3.

As shown by results, a well resolved peak shift was obtained even in the case of small concentration of the pesticide (i.e., 0.5 or 1 ppm). The shift increased with concentration until saturation at about 33 ppm, which is the solubility limit of atrazine in water. For low concentrations of the pesticide (0–5 ppm), the sensor response was linear, and we could calculate the sensitivity of the sensor as the slope of the linear curve interpolating the experimental points. Thus, we obtained the values of 1.19 (3) nm/ppm and 0.51 (2) nm/ppm for aqueous and humic solution, respectively. From these numbers, we also estimated the limit of detection (LOD), in both cases, as the ratio between the instrument resolution and the sensitivity. LOD numerical values have been reported in the inset of Fig. 3.

5. Conclusions

We have presented a simple and well performing optical microsensor of pesticides, based on the simple and low-cost porous silicon nanotechnology. The device has a normal-to-the-surface microcavity structure that is directly realized on the silicon chip by electrochemical etching. The fabrication process is compatible with silicon microelectronic and micro-machining technologies, so that the sensors could be monolithically integrated with microelectronic circuits, or be part of a microsystem.

In terms of measurement resolution, the resonant cavity enhanced operation of the proposed sensor offers very good performances: the interaction between the porous silicon microcavity and the external fluid de-tunes the optical microcavity inducing large shifts of its resonant peak wavelength.
Sensitivities as low as 1.2 and 0.5 nm/ppm, respectively, for aqueous and humic solution containing atrazine have been measured.

In our experiments, the sensor output is usually monitored by an optical spectrum analyzer. Anyway simpler and cheaper experimental configuration can be thought based on the on/off behaviour of the sensor when it is interrogated at a single wavelength (e.g., the resonant wavelength).

We finally note that the device, in the present form, can be only used in monitoring single pesticide contaminated solutions, such as it is, for instance, required in the quality control of mineral waters. Anyway, the proposed sensor can be thought of as a possible building block in a quantitative sensor array system, using polymer membranes selectively permeable to different pollutants (Pinnau, 2004), capable of sensing at the same time without interferences complex pesticide mixtures of environmental interest. Therefore, we believe that the proposed technology could be of great interest in the next development of commercial sensors of pesticides in liquid solutions.

References


