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ELECTROCHEMICALLY CONTROLLED OPTICAL WAVEGUIDE SENSORS

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Introduction

Optical techniques are at the forefront of modern analytical methods due to their inherent high specificity. From the point of view of sensor technology, the transfer of chemical information into a measurable signal is of utmost importance. In this respect, planar optical waveguides show great promise for realising novel chemical and biological sensors which use evanescent fields to probe specifically sensitised films on the waveguide surface. Such sensors may detect changes in the refractive index of films using, for example, surface plasmon resonance (SPR) [1], light emission from the binding of proteins labelled with fluorophores [2], or the change in absorption spectrum of a film caused by a chemical reaction [3]. The use of photolithography in integrated optics technology allows mass production of complex multisensors on small and robust substrates. Electrochemical methods allow electrical resetting of reactions, or improved sensitivity through phase-sensitive detection.

The present work comprises the demonstration of two types of sensors based upon:

(a) Evanescent field spectroscopy, and
(b) Waveguide-coupled surface plasmon resonance.

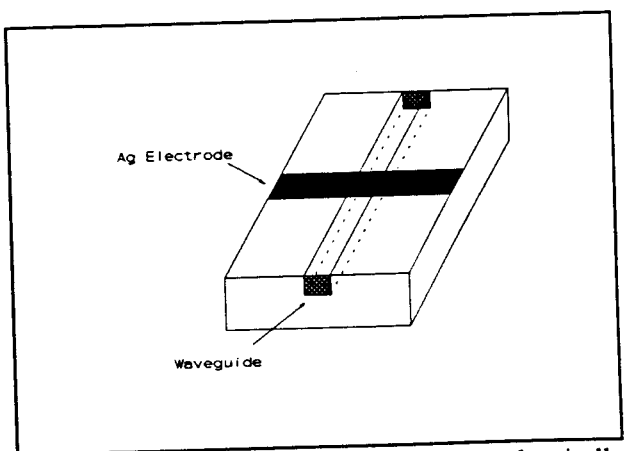

Figure 1 Schematic diagram of the electrochemically modulated Surface Plasmon Resonance device.

Experimental

(a) Device fabrication

The waveguides used for both devices were prepared in the same way. Single-mode channel waveguides were fabricated in a soda lime glass substrate by ion-exchange in molten KNO_3 at 392°C for 1 hour [4].

In the case of the device based on evanescent wave spectroscopy, a 200 nm thick silica film was deposited on the waveguides by RF sputtering in an argon atmosphere. A 10 nm thick ITO film was then deposited by reactive evaporation in oxygen and was annealed in an atmosphere of cracked ammonia [6]. The sheet resistance of this film was 730 ohms/square.

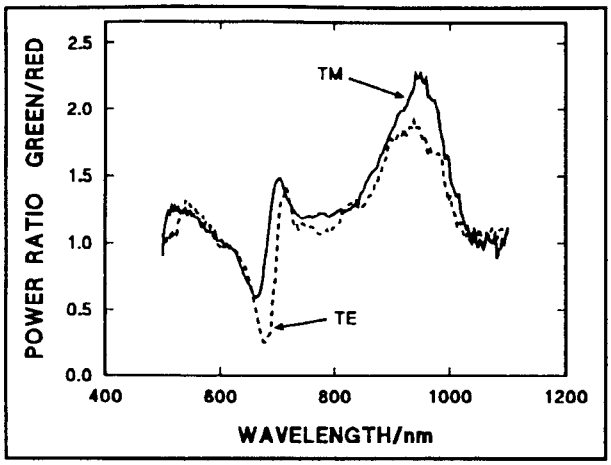

Figure 2 Wavelength dependence of the transmitted power ratio of the green/red $Lu(PC)_2$ sensing film for different polarizations.

For the SPR device, a 40 nm layer of Ag was deposited directly onto the waveguide, covering a 5 mm length of it. In both cases, electrical connection to the surface film was by means of silver loaded epoxy.

The first device was configured as a chlorine sensor by depositing by vacuum evaporation a 10 nm thick layer of lutetium biphthalocyanine ($Lu(PC)_2$) to cover 4.5 mm length of the waveguide [5]. $Lu(PC)_2$ is readily oxidised by chlorine, strongly changing its absorption spectrum. The SPR device was of similar construction but with the SiO_2 and $Lu(PC)_2$ films omitted, and the ITO replaced with a Ag film. A schematic diagram of this sensor is shown in Figure 1. In each case a silica cell of inner diameter 12 mm and a height of 16 mm was attached to the substrate surface with silicone rubber. A silver/silver chloride reference electrode and a platinum counter electrode were placed in the cell for electrochemical control of the state of the surface film. Facilities were included for the deaereation of the solutions.

Device Operation

(a) Evanescent Wave Spectroscopy

Chlorine sensing was carried out by allowing the $Lu(PC)_2$ film to chemically react with dissolved chlorine for a fixed length of time (10 minutes). After this period, the partially oxidised film was electrochemically reset by applying a suitable reduction potential to the ITO layer with respect to the Ag/AgCl electrode. The transmission properties of the waveguide were measured using light from a white light source, passed through a monochromator and coupled to the waveguide using a single mode fibre. Transmission is strongly dependent on the oxidation state of the film [4,5], as shown in Fig. 2, where the ratio of the transmitted power for the oxidised and reduced states of the $Lu(PC)_2$ film are showed for

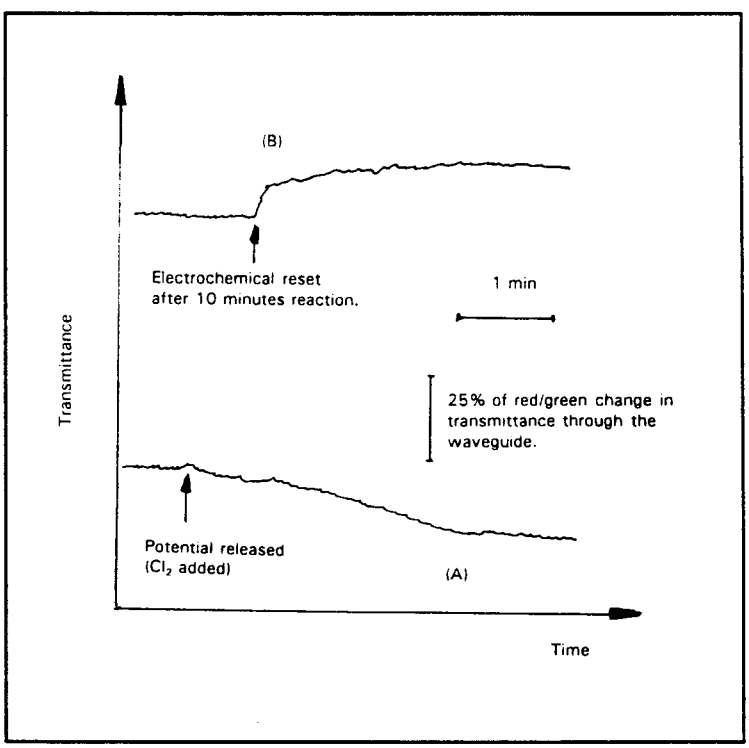

Figure 3 Time dependence of power transmittance through the optoelectrochemical device: (A) After addition of 10 ppm of Cl_2, and (B) After electrochemical reset.

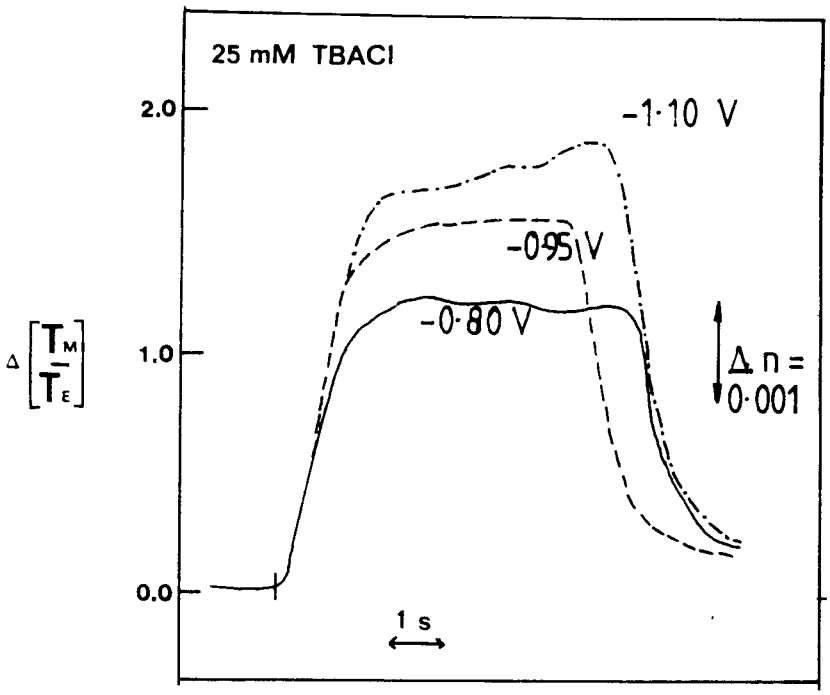

Figure 4 Time dependence of the ratio T_M/T_E for power transmitted through the SPR device for different potential steps, from -0.4 V to the values indicated.

both the TE and TM modes. The changes in power output for the TM mode at 950 nm were used for monitoring Cl_2 concentration and a resolution limit of approximately 1 ppm was achieved. An example of the changes of transmission on reaction of the film with chlorine and subsequent electrochemical reset is shown in Fig. 3.

Although this device and its associated signal processing and operation is not optimized, these results confirm that electrochemical modulation can be coupled to planar waveguide technology for the manufacture of sensing devices.

(b) Waveguide coupled Surface Plasmon Resonance.

The integrated optical realisation of an SPR sensor reported in this paper relies upon the phenomenon of coupling between a surface plasma wave (SPW) at the metal/analyte interface and the TM mode of a planar optical waveguide. The metal overlayer is used as an electrode in this optoelectrochemical device. Monochromatic light at 632.8 nm is coupled into an ion-exchanged optical waveguide onto which a thin silver film has been deposited. In terms of coupled modes, the velocity of the SPW at the silver/analyte interface depends strongly upon the refractive index of the analyte solution, within approximately 0.1 nm of the interface, whereas the velocity of the waveguide mode is not significantly affected by the index of the analyte. When these velocities are equal, significant power is coupled from the low loss waveguide mode into the high loss SPW, resulting in a substantial reduction in the waveguide output power. As the surface plasmon wave is only supported in the TM polarisation, the waveguide TE mode is largely unaffected and may be used as reference signal for the sensor.

Theoretical considerations show that for this simple device resonance occurs at a bulk solution refractive index of 1.42. This has been experimentally verified with ethylene glycol

- water solutions, providing an accurate calibration curve.

The great sensitivity of this device to small refractive index changes in a small thickness layer makes it ideal as an electrochemically-modulated sensor. The sensitivity of the device to the chemical composition at the interface was tested by studying electrochemically controlled adsorption of tetrabutylammonium ion (TBA) on silver. Figure 4 shows the large changes in the ratio of transmitted power TM/TE on applying potential pulses to the Ag surface. It must be emphasised that these large changes in optical signal are due to changes of less than monolayer coverage of the surface, highlighting the possibilities of combining waveguide coupled SPR with electrochemical methods, in particular, the feasibility of electrochemical resetting of the active surface.

Conclusions

Two examples of a new family of optoelectrochemical transducers are given, demonstrating great potential for sensing applications. There are three main advantages in this approach: (a) Integration of optical and electrochemical multisensors in a single planar optical chip, (b) Electrochemical modulation, which allows resetting and self calibration of the devices, and (c) Additional information sensitivity due to the combination of these two techniques.

References

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