Sensors and Actuators A, 25–27 (1991) 449–452

Design and Realization of a Surface Plasmon Resonance-based Chemo–Optical Sensor

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Abstract

Surface plasmon resonance is applied for sensing concentrations of ammonia in air, using a thin bromo-cresol purple layer as a chemo–optical interface. The sensor shows a dynamic range of 0.5–15 mbar, a resolution of about 5% and a response time smaller than 1 min.

Introduction

Sensing chemical concentrations by optical means offers some specific advantages, such as no electromagnetic interference, no danger of explosion and often a high sensitivity. For fast *in situ* measurements intrinsic evanescent field sensors [1] are very promising. In these sensors chemical concentration-induced changes in optical properties are probed by light propagating through a light guide, by virtue of the small part of the corresponding electromagnetic field travelling outside the guiding laying. Both optical fibres and planar waveguides, known from integrated optics [2], can be used as light guides. If the sensing principle requires optical conditioning of the input light and optical processing of the light coming out of the sensing waveguide, integrated optical sensors, in which all required functions can be realized simultaneously, have preference. The sensing structure based on surface plasmon resonance (SPR) presented here can be included in both fibre-optic and integrated-optic sensors.

In evanescent field chemo–optical sensors the leading part is played by a thin interface layer. In this layer a change in the concentration of a chemical species, X, in the environment is transduced into a change of optical properties of the interface layer, such as the luminescent ones or the refractive index $\tilde{n}$. This transduction function can be implemented by immobilizing molecules A in the interface layer, which associate reversibly with X:

$$\mathrm{A} + \mathrm{X} \overset{K_{\mathrm{ass}}}{\rightleftharpoons} \mathrm{AX}$$

Molecules A have to be found or designed which show a large enough difference in the relevant optical properties between both extreme states $[\mathrm{A}] = 0$ and $[\mathrm{AX}] = 0$ of the interface layer. These concentration-induced changes of the optical properties of the interface layer in turn have to be read out, which is usually realized by transducing them into light intensity changes by applying proper optical principles.

The design of these A molecules is governed by the requirements of the application in question, such as the resolution, dynamic range, speed and selectivity [3]. In most cases the resolution, as far as it originates from the A molecules, is determined by differences in the energy-level schemes of A and AX. The dynamic range is defined by K_{ass} and the resolution, and the speed by the rate constants of the complexation and decomplexation reactions. Of course, the resolution will also depend on the total concentration $[\mathrm{A}] + [\mathrm{AX}]$ in the interface layer, the dimensions of this layer and the optical part of the sensor.

In order to obtain fast sensors, the thickness of the interface layer has to be small, preferably in the range 1–20 nm; the SPR

Elsevier Sequoia/Printed in The Netherlands

method is shown to be very appropriate [4] for measuring the optical properties of these thin layers.

Sensing by Surface Plasmon Resonance

The basic element of an SPR-based chemo-optical sensor is presented in Fig. 1(a). A guided wave, the so-called surface plasmon (SP) [5], can propagate along the surface of a layer which has a negative real part of its dielectric constant, such as silver or gold. Its light energy is confined to the interface of the materials on both sides of the SP-guiding surface. This light confinement is indicated in Fig. 1(b) by presenting the x-dependence of the magnetic field H_y of an SP propagating in the z-direction.

The properties of this SP, especially its propagation constant β_{SP} (defining the periodicity of the wave in the propagation direction), are strongly dependent on the refractive indices of the materials through which the SP propagates. Because a large part of the energy propagates through the interface layer, β_{SP} is very sensitive to small changes of $\tilde{n}$ in this layer. It is much more sensitive than the propagation constants of light modes travelling through optical fibres or planar waveguides with this interface layer. The β_{SP} value can be read out by offering the basic sensing element a continuous spectrum of β-values from which the one equal to β_{SP} will be extracted. Its energy is used for mode-coupling-based excitation of the SP. A specific example of this method [6] is presented in Fig. 2, where the β-values are offered from a waveguide; this method is highly applicable in microsensors. Note the broadening of β_{SP} into a dip caused by the imaginary parts of the refractive indices, which reflects the absorbing properties of the layers. Larger broadening will result in lower resolution, because then β_{SP} can be read out less accurately.

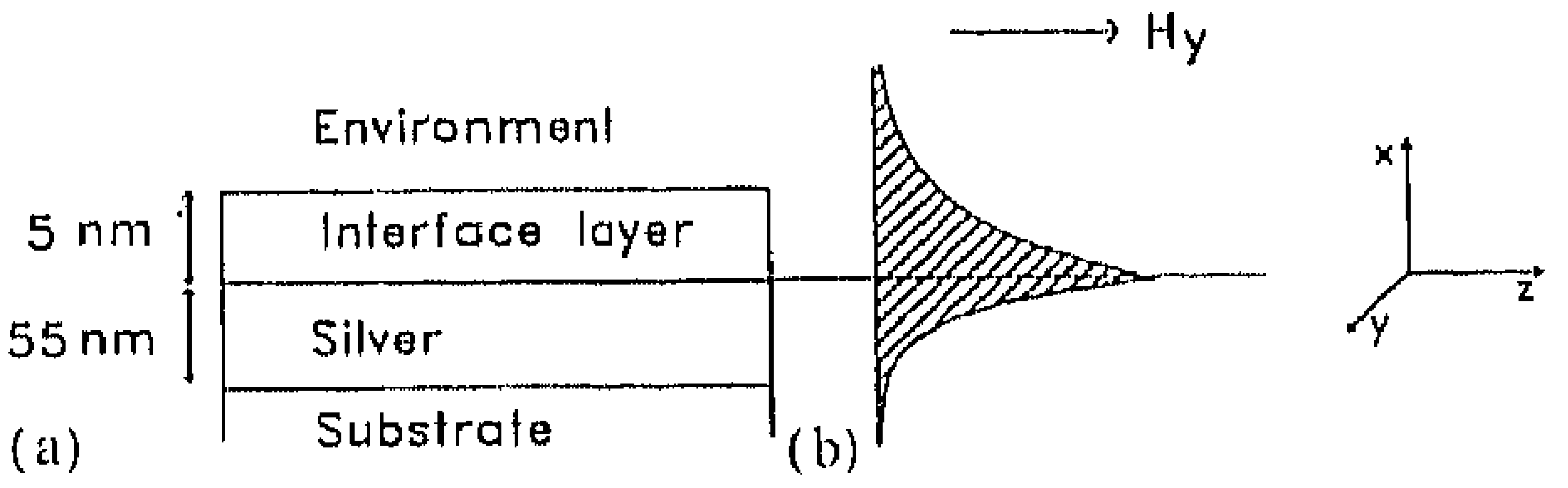

Fig. 1. Basic element of an SPR-based chemo-optical sensor (a) and x-dependency of the magnetic field H_y, of the SP propagating through this element (b).

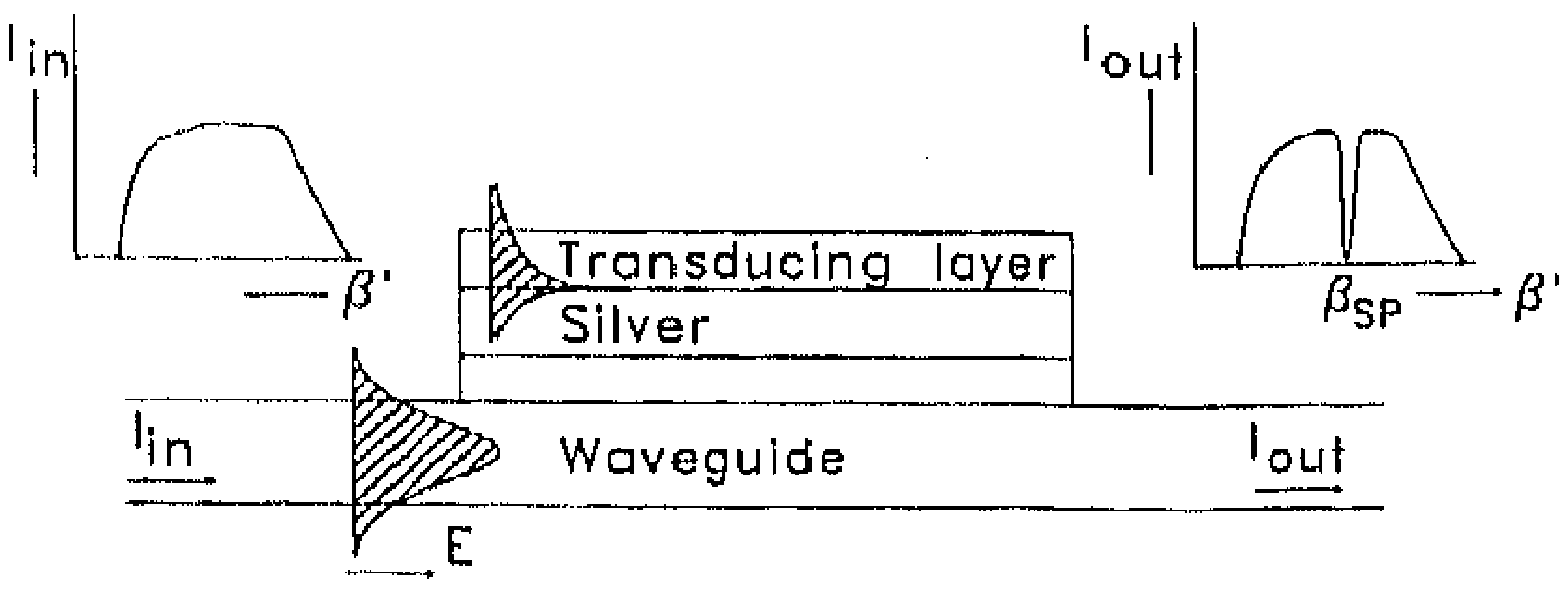

Fig. 2. Excitation of a surface plasmon from a waveguide.

Experimental

The investigated SP supporting structure is depicted in Fig. 3, together with the functions of the various layers. This structure is optimized by computer simulations in order to obtain the maximum resolution, defined as $\Delta\beta_s^0/\Delta\beta_n$, where $\Delta\beta_s^0$ represents the maximal shift of β, and $\Delta\beta_n$ the inaccuracy of the β-measurement [3]. This structure has not been produced on a waveguide (Fig. 2) but on a glass slide, thereby obtaining an easy method for characterization of its sensing properties by the use of the Kretschmann method [7].

In this illustration of the SPR principle we did not apply an optimally designed interface layer, but rather a thermally evaporated bromo-cresol purple (BCP) layer, BCP being

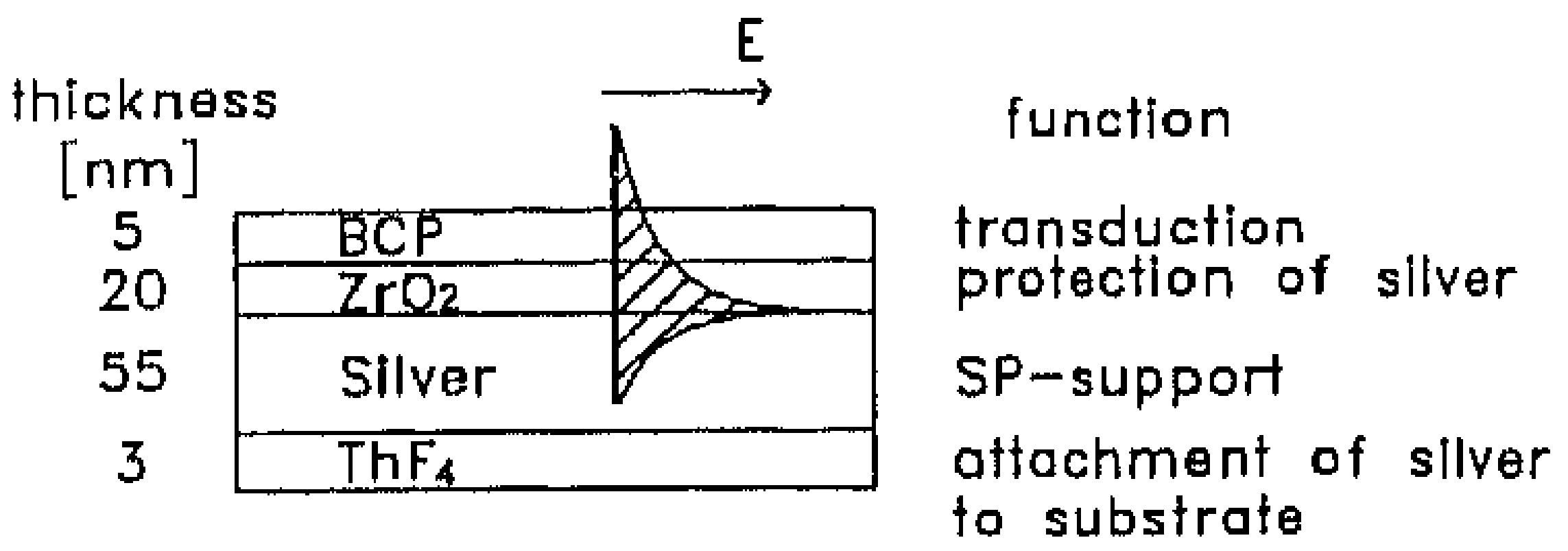

Fig. 3. SP supporting structure, showing thickness and function of the layers.

a well-known pH indicator. The chemo-optical transduction is based on the chemical equilibrium reaction:

$$\underset{A}{BCP} + \underset{X}{NH_3} + H_2O \rightleftharpoons \underset{AX}{BCPOH^- . NH_4^+}$$

Both states of the BCP, A and AX, show large differences in both the real and imaginary parts of the wavelength-dependent refractive index ($\tilde{n} = n' + jn''$) (Fig. 4). Because the sensing is based on n' changes and high n'' values have to be avoided, a good wavelength region will be $\lambda > 700$ nm; we have chosen $\lambda = 712$ nm.

The β_{SP} shift as a function of the partial pressure of NH_3 (P_{NH_3}) is presented in Fig. 5. Defining α as the BCP fraction in the complexed state and assuming n to be a linear function of α, it can be deduced [3] that

$$P_{NH_3} = c_1 \frac{\beta_{SP} - \beta_{SP}(\alpha = 0)}{\beta_{SP}(\alpha = 1) - \beta_{SP}}$$

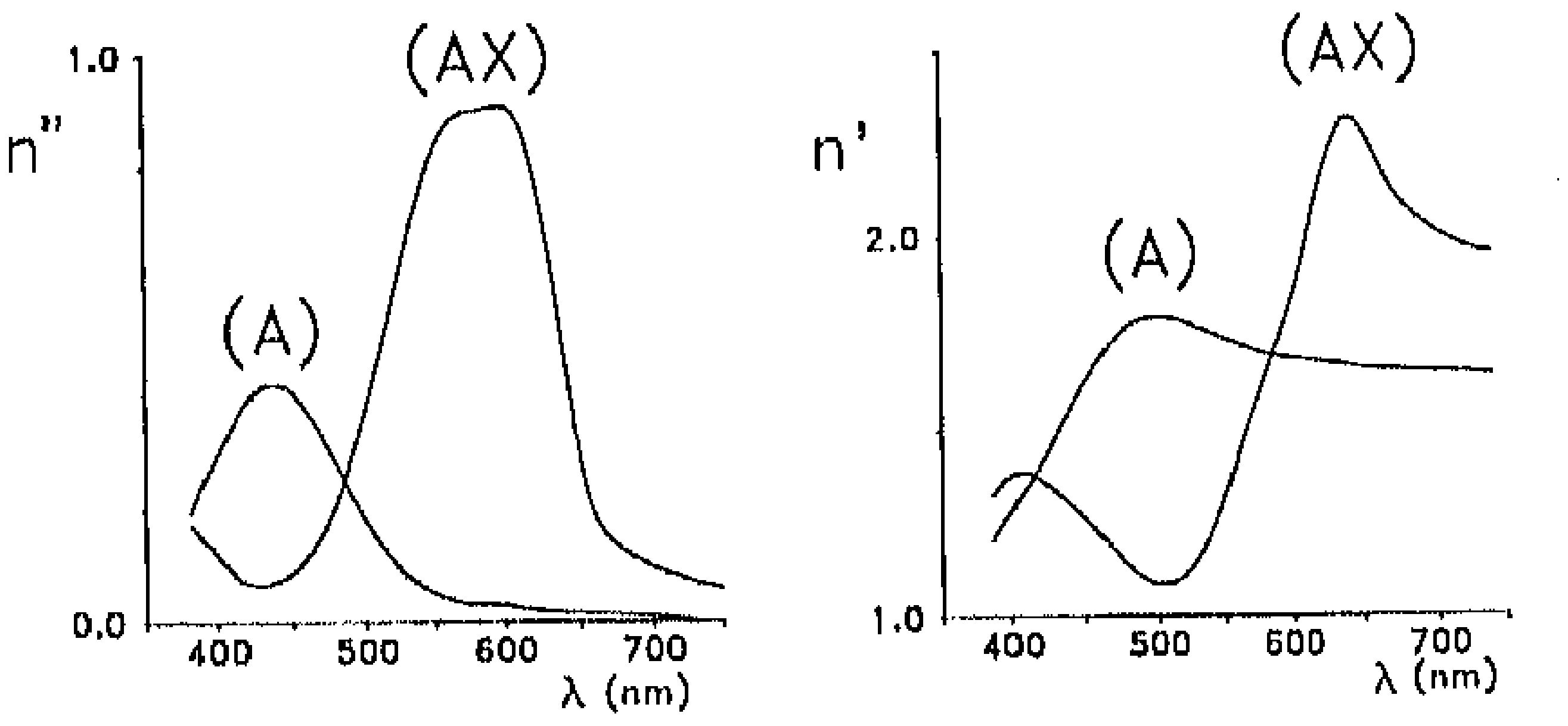

Fig. 4. The real (n') and the imaginary (n'') parts of the refractive index of BCP.

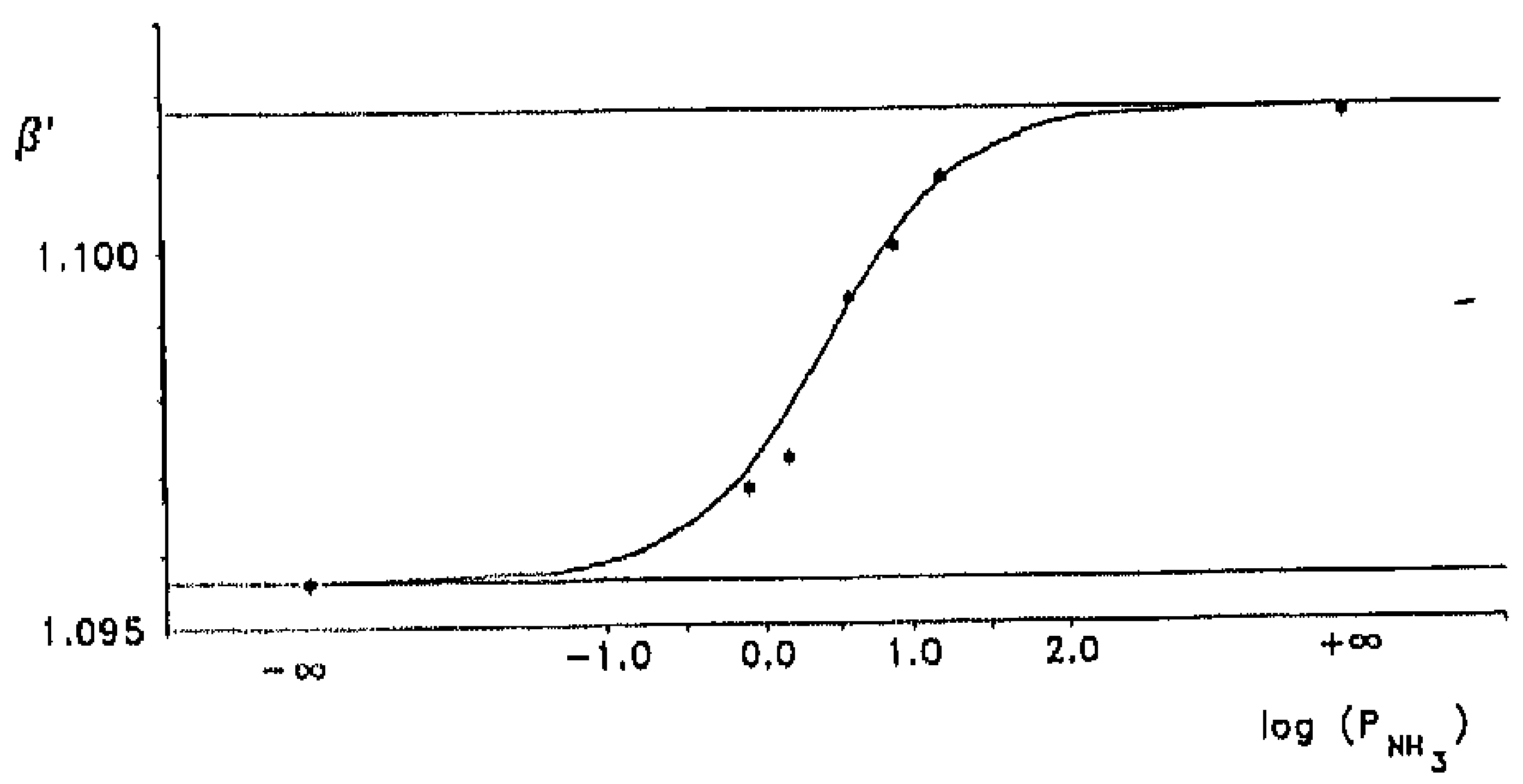

Fig. 5. β'–$\log(P_{NH_3})$ relation (β' in units of $2\pi/\lambda_1$, $\lambda_1 = 712$ nm, P_{NH_3} in mbar): ——, simulated; *experimental.

TABLE 1. Performance of the NH_3 sensing part

Dynamic range	0.5–15 mbar
Resolution	~20 steps
Selectivity	none
Response time	<1 min
Reproducibility	good
Stability	>6 months

By fitting c_1 (best value 2.7 mbar), a good correspondence between theory and experiment is obtained. The performance of the sensor is presented in Table 1. The resolution is obtained from computer simulations assuming that the intensities can be measured within an inaccuracy of 1% full scale. The sensor is expected to show no selectivity, but may be sensitive for the presence of other pH-changing gases such as CO_2, SO_2 and H_2S. In order to obtain selectivity and to match the properties to the use of cheaper light sources, special molecules have to be designed and synthesized, e.g., chromo-ionophoric molecules consisting of crown ethers as the ionophoric part and merocyanine dyes as the chromophoric part [3]. We expect that the resolution of the SPR sensors can be greatly improved using more complicated sensor structures.

Conclusion

An SPR-based NH_3 sensor shows a promising performance and great improvements are expected in the future.

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