A SURFACE PLASMON RESONANCE BASED AMMONIA SENSOR

J. v. Gent, P.V. Lambeck, R.J. Bakker, E.J.R. Sudhölter, D.N. Reinholdt and Th.J.A. Popma

University of Twente, Departments of Electrical Engineering, Organic Chemistry and Applied Physics, P.O. Box 217, 7500 AE Enschede, The Netherlands, N1N790, 7p, IN990, HL7990, OK990(?)

The Surface Plasmon Resonance method for sensing chemical concentrations is dealt with shortly. The structure and performance of the sensing part of an SPR-based ammonia sensor is presented.

INTRODUCTION

A promising method for sensing chemical concentrations by optical means is the Surface Plasmon Resonance method (SPR) [1-6], based on the excitation of a particular type of guided mode, the Surface Plasmon (SP) mode. In fact this mode does not travel through a waveguide, but along the surface of certain materials such as silver or gold. The light energy of this SP appears to be confined to two thin material slices, one on each side of the surface. The corresponding magnetic field decays on each side exponentially with the distance to the surface, with decay constants of < 0.5 μ (fig 1).

Most chemo-optical waveguide sensors are based on an optical readout of concentration-induced changes of the refractive index n of a thin layer, viz the chemo-optical transduction layer. An interesting readout method can be obtained by positioning the transduction layer on
\[ \vec{H}_{1,2}(x,y,z,t) = e^{-\alpha_{1,2} |y|} e^{i(\omega t - \beta z)} \]

Fig. 1. The magnetic field of a Surface Plasmon

top of a waveguide structure. In this case the fields of the guided modes will extend over that layer, making the mode properties and especially the propagation constant \( \beta \), sensitive for changes in the refractive index of the transduction layer. Here the strong point of using an SP reveals its specific field profile (fig 1), by which a relatively large part of the light energy will propagate through the transduction layer. Therefore the \( \beta(\mathbf{r}) \) dependence will be strong, exceeding that of the three-layer waveguides by more than an order of magnitude (see fig 2).

For measuring its propagation constant \( \beta_{sp} \), the SP has to be excited, by taking energy from other modes, whether radiation modes (Kretschmann method, see [6]) or guided modes [2]. The condition for this is that (components of) the propagation constant of both modes involved at the energy transfer are equal.

Thus \( \beta_{sp} \) can be measured by offering a spectrum of \( \beta \)-values and observing which \( \beta \)-value has been extracted from them, its energy being used for SP excitation (fig 3). Due to absorption of light in the silver layer, the SP will be strongly damped, causing a broadening of this extracted \( \beta \)-value to a band around \( \beta_{sp} \). Here we reporta
Fig. 2. Magnetic field profiles for Surface Plasmon (a) and waveguide (b)

transduction layer

field in the transduction layer

Fig. 3. Excitation of a Surface Plasmon from a waveguide

representative example of the sensing part of an SPR-based sensor, being capable of measuring ammonia concentrations [3].

EXPERIMENTAL PART

The investigated SP supporting structure is given in fig.4. This structure can be realized on a glass slide, as is required for the application of Kretchmann’s measuring method, as well as on top of a
Fig. 4. SP-supporting structure, showing thickness and function of the layers

waveguide, as has to be done in order to obtain a small sensor system (fig 3).

The chemo-optical transduction is based on the chemical equilibrium reaction:

\[
BCP + NH_3 + H_2O \rightleftharpoons BCFOH^- \cdot NH_4^+
\]

Both states of the Bromo Cresol Purple, the complexated and the uncomplexated one, show large mutual differences in both the real part \(n'\) and the imaginary part \(n''\) of \(\bar{n}\) (see fig 5). The SPR sensing principle is based on the \(\delta_{sp}(n')\) dependence, \(n'\) being determined by the \([NH_3]\)-dependent BCP/BCFOH\(^- \cdot NH_4^+\) ratio. Large \(n''\) values have to be avoided, because they would result in a strong decrease in the accuracy of the \(\beta'\)measurement. Fig 5 shows a large difference in \(n'\), together with small \(n''\)-values in the wavelength region \(\lambda \geq 700\) nm; we have chosen a \(\lambda = 712\) nm layer [7]. The \(\beta'(pNH_3)\) dependence of the structure, obtained by using Kretchmann's method is presented in fig 6. Defining a
Fig. 5. The real ($n'$) and the imaginary ($n''$) part of the refractive index of BCP.

Fig. 6. $\beta'$-$\log (P_{NH_3})$ relation ($\beta'$ in units of $2\pi/\lambda_i, \lambda_i = 712\ nm, P_{NH_3}$ in mbar) ——— simulated, * experimental
as the BCP-fraction in the complexated state and assuming \( n' \) to be a linear function of \( \alpha \) it can be deduced [3]:

\[
p_{\text{NH}_3} = C_1 \cdot \frac{\beta'_{sp} - \beta'_{sp}(\alpha=0)}{\beta'_{sp}(\alpha=1) - \beta'_{sp}}
\]

A good correspondence between theory and experiment is obtained for \( C_1 = 2.7 \) mbar.

Starting from the assumption, that the intensities can be measured with an inaccuracy of 1 %, the resolution can be calculated, using proper simulation programs [3]. Because BCP is a PH-indicator, the sensor is expected to show no selectivity, but may also sense other gasses. Selectivity might be obtained by chemically binding the BCP molecule to a proper ionophore, such as a crown ether [3]. We expect that the resolution of the sensor can be strongly improved by using more complicated sensorstructures.

Conclusion

An SPR-based \( \text{NH}_3 \)-sensor shows a good performance, and it is expected that great improvements will be possible in the future.

References

1. B. Liedberg, D. Nylander, I. Lundström
   Surface Plasmon Resonance for gas detection and biosensing,
   Sensors and Actuators 4 (1983) 299
2. H.J.M. Kreuvel Planar waveguide sensors
   Ph.D. Thesis, University of Twente, the Netherlands 1988

3. J. van Gent Surface Plasmon Resonance based chemo-optical sensors.
   Ph.D. Thesis, University of Twente, the Netherlands 1990.

4. J. van Gent, P.V. Lambeck, H.J.M. Kreuvel
   Th.J.A. Popma, E.J.R. Sudholter, D.N. Reinhoudt

5. R.P.H. Kooyman, H. Kolkman, J. van Gent, J. Greve
   SPR-immunosensors: sensitivity considerations.

6. J. van Veen, Optical bio-sensors, these proceedings (1990)

7. P.V. Lambeck, Integrated Optic chemical sensors,
   these proceedings (1990)