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# SURFACE PLASMON DISPERSION AND LUMINESCENCE QUENCHING APPLIED TO PLANAR WAVEGUIDE SENSORS FOR THE MEASUREMENT OF CHEMICAL CONCENTRATIONS.

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## Abstract.

Two novel types of planar waveguide sensors for the chemical domain are introduced. Both are realized by thin film technologies. They consist of multilayered structures coated by a very thin organic overlayer that is able to absorb the species to be measured out of the environment. This absorption results in a change in its dielectric function. In the first sensor to be demonstrated this change is measured using a surface plasmon mode as a probe. In the second one the radiationless energy transfer from luminescent centres incorporated in one of the layers to the overlayer serves as a probe.

## 1 INTRODUCTION.

In general the central part of solid-state optochemical transducers is formed by a material that by virtue of its capacity to absorb the entities to be measured, translates a variation of a chemical concentration into a variation of its dielectric function  $\hat{\epsilon}(\omega, r)$ .

At the atomic level this change may arise from a wide variety of interactions between light and matter.

As compared to other types of transducers optochemical ones are especially attractive when materials can be applied where these changes in  $\hat{\epsilon}$  are strongly manifest at certain wavelengths.

Waveguides form a very attractive means to probe such changes as the feature of well-defined discrete modes combined with a high concentration of the electric and magnetic fields will result into very effective sensing principles.

In the following sections two new types of waveguide sensors are introduced, both relying on a wavelength dependent change in the dielectric function of an organic layer having a nominal thickness of 10 nm. that is placed on top of a multilayered structure. This layer shows wavelength dependent absorption due to electronic transitions. The strength and position of these transitions varies as a result of the chemical absorption of the measurand giving a change in  $\hat{\epsilon}$ .

The first type of sensor demonstrated, (the S.P.W.-Sensor) exploits the dispersive side effects of the electronic transitions. A surface plasmon (S.P.) is used to probe the real part of  $\hat{\epsilon}$  of the overlayer.

The second type, (the LUQUEN-Sensor) probes the  $\hat{\epsilon}$  changes by measuring the amount of quenching of luminescent light emitted by centres incorporated in one of the layers of the guiding structure.

Before describing these sensors some attention will be paid to the development of the ion-sensitive overlayers we intend to use as transducing interfaces.

## 2 Ion-sensitive overlayers exhibiting colour changes.

The interface between the optical transducer system and its chemical environment is realized by a coating placed on top of a multilayered planar waveguide structure. In order to realize chemically sensitive overlayers a new kind of chromoionophore is being developed. These molecules consist of two functional groups. The first one, the ionophoric group (upper part of fig.1.) can complex with a cation, eg.  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ . The second one, the chromophoric group (a cyanine dye, lower part of the molecule) is responsible for the colour of the molecule. Complexation can cause the dissociation of the phenolic OH. The resulting change in the electronic structure of the chromophoric group will change the colour of the molecule giving a change in  $\epsilon$ . Fig.2 shows the absorption spectrum of a cyanine dye. Kramers-Kronig relations are used to calculate the dependency of the refractive index from this absorption spectrum.

## 3 A Surface Plasmon Waveguide Sensor.

In this type of sensor the mode feature of the waveguide plays an essential role in the modulating mechanism. A Surface Plasmon (S.P.) is used to probe the real part of the dielectric function of an organic coating of the type described above. A change in this will modulate the constant of propagation of the S.P. mode which is detected using wavelength dependent coupling with a normal waveguide mode. An S.P. is an elementary excitation at a metallic surface showing a hybrid character, i.e. partly photon, partly plasmon-like. An S.P. mode travelling along the interface of a metal and a dielectric material is a regular solution of Maxwell's equations and originates from the negative

dielectric function of the metal.

The electric field of a S.P. wave that propagates in the z-direction varies as:

$$\hat{E}(x, z, t) = \hat{E}(x) \cdot \exp(j(\hat{\omega} t - N_{\text{eff}} \cdot k_0 \cdot z)) \quad \text{with} \quad k_0 = 2\pi / \lambda \quad (1)$$

Complex quantities appear because of the complex dielectric function of the metal. The change in the S.P. constant of propagation arising from a local change in  $\epsilon(\omega, r)$  can be derived using the variational theorem for dielectric waveguides<sup>2</sup>.

$$\delta N_{\text{eff}} = \frac{c}{P} \int \Delta \epsilon(\omega, r) \cdot |\hat{E}|^2 dx \quad (2)$$

Here c symbolizes the vacuum light velocity and P the power carried by the mode.

In a preliminary study the organic overlayer was simulated by a gelatine film having a nominal thickness of about 3 nm. and a refractive index of about 1.54. Because gelatine is able to reversibly absorb water the exact thickness depends on the humidity of the environment.

Fig.3 shows that part of the multilayered structure that guides the S.P. mode. This mode is excited at the silver-zirconia interface. Silver is used as the plasmon active material because of its low damping as compared with other metals. The thickness of the zirconia layer is tuned to give a maximum strength of the electric field in the organic sensing layer in order to optimize the sensitivity. The titania layer was applied in order to prevent coupling with an additional S.P. mode that would otherwise be excited at the silver-silica interface. The refractive indices indicated are taken from literature. The complex constant of propagation  $N_{\text{eff}}$  characterizing the S.P. mode as well as the complex field vectors  $\hat{E}(x)$  are calculated by a numerical solution of Maxwell's equations for the structure indicated in fig.3.

Also drawn in fig.3 is the distribution of  $|\hat{E}|$  that was calculated taking  $\lambda = 600$  nm. The 50-nm. bar indicates the vertical dimensions. Note the strong field confinement as compared to the more familiar dielectric modes. It is this strong confinement that makes an S.P. mode a powerful probe in studying interface properties<sup>3</sup>.

Fig.4 shows a schematic cross-section of the whole transducer revealing its performance. It is composed of a three-layer waveguide (a Silicon-Oxygen-Nitride core embedded in between a substrate and a cladding of silica, hereafter called the SiON waveguide) that was modified over a distance of  $100 \mu\text{m}$ . by placing the structure of fig. 3 on top of it.

Fig.5 shows the dispersion curves of the modes propagating in the entire structure. For the S.P. mode two curves are drawn, with and without a gelatine coating (3 nm. thick). These curves are calculated using the refractive indices indicated in fig.3. Polychromatic light from a halogen source was excited in the TM mode of the SiON guide using a prism coupler. Photons having almost equal constants of propagation in SiON and S.P. modes transfer cumulatively to the latter, where they are damped. The coupler acts as a wavelength-selective absorption filter.

Fig.6 gives the filter functions appertaining to the structure with and without a gelatine coating as determined from experiment.

The functions<sub>3</sub> are also given that are calculated by theory based on a leaky-wave approximation.

As for the position of the absorption maxima, correspondence between theory and experiment is satisfying but the widths of the experimental functions are quite large. This could be due to surface roughness. Ideally the width only depends on the imaginary part of the dielectric function of the metal.

The sensor behaviour of the filter is demonstrated by putting a damp finger close to the coating. The centre wavelength shifts about a hundred nanometers. More quantitative experiments on the humidity sensitivity of the sensor are in progress.

Up till now the performance of the sensor when using organic overlayers of the type described in section 2 has only been studied theoretically. An overlayer of 5 nm. thickness was taken with a concentration of 1 Molar cyanine molecules.

Fig.7 shows the dispersion behaviour of the S.P. mode that propagates in the structure of fig.3 where the gelatine is now replaced by this overlayer. Two distinct curves are indicated, the difference results from a shift in the absorption of the chromophore of 10 nm. In practical situations we expect this shift to be much larger.

The shaded area indicates the damping of the S.P. wave and is related to the imaginary part of its constant of propagation. For the state of clarity this is only indicated for one of the curves.

From these computer simulations we conclude that the S.P. excitation couples with the electron transition in the overlayer giving strong anomalies in its dispersion behaviour. This coupling of S.P. waves with exciton states has been described elsewhere<sup>4</sup>.

In the wavelength region where strong coupling occurs the details of the dispersion curve, eg. a shift resulting from a shift in the absorption spectrum of the cyanine, are masked by the damping. Only at wavelengths in the dispersive side band of the cyanine

absorption line (at about  $\lambda = 680$  nm.) the sensor can discriminate between the two configurations of the chromoionofore for the situation given.

#### 4 A LU(minescence) QUEN(ching) Sensor.

In the second type of sensor we demonstrate, the transducing principle is not based on a waveguiding property although the waveguide plays an essential role. The strong coupling between the fields of a mode propagating in a multilayered structure and the near field of (photo)luminescent centres incorporated in one of its layers will result in a high excitation efficiency of these centres as well as a high detection efficiency of the light subsequently emitted.

The modulating mechanism itself is based on the radiationless energy transfer between the luminescent centres (donors) and quenching centres (acceptors) in the surface coating. In many luminescent materials the energy of an excited state (exciton) can transfer continuously from one luminescent centre to the other by dipole-dipole interactions until it will finally be emitted as a photon. This exciton transfer is interrupted suddenly if the exciton enters a site at which it can transfer its energy to another type of centre (the acceptor) that decays immediately to its ground state in a radiationless way. As a result no photon will be emitted and the luminescence is quenched. The amount of quenching will be controlled by four transfer rates:

-The donor-acceptor transfer rate  $k_{da}$ .

According to Förster the transition rate for an electric dipole process in which a donor transfers energy to an acceptor can be written in terms of the luminescent line-shape of the donor  $f_d$  and the absorption line-shape of the acceptor  $F_a$

$$k_{da} = \frac{3H^4 Q_a}{4\pi R^6 n^4 \tau_d} \int \frac{f_d(E) \cdot F_a(E)}{E^4} dE \quad (3)$$

In this expression,  $Q_a$  is the integrated absorption cross-section,  $\tau_d$  is the radiative lifetime of the donor luminescence, and  $R$  the mutual distance.

-The donor-donor rate  $k_{dd}$ .

This transfer is identical to the first one if the donor absorption and emission spectra show overlap.

-The spontaneous decay rate of a single donor  $k_d$ .

-The spontaneous decay rate of a single acceptor  $k_a$ .

The LUQUEN sensor is based on the detection of the donor quenching rate,  $P_{\text{quench}}$ , as a measure of  $k_{da}$ . The latter becomes modulated when the absorption behaviour of the overlayer changes. The acceptor sites are incorporated in the overlayer. If  $k_{dd}$  is much larger than either  $k_d$  and  $k_{da}$ , the donor excitation becomes uniformly distributed over all available sites. In this limiting situation of very fast exciton migration all donor sites become equivalent and we can define a geometrical factor  $f$  as the ratio of the number of acceptor sites near a donor to the total number of complexing agent molecules. In this situation the probability of an exciton becoming quenched at an acceptor site is given by

$$P_{\text{quench}} = \frac{f \cdot k_{da}}{k_d + f \cdot k_{da}} \quad (4)$$

This quenching rate is the sensor output. Because  $f$  is proportional to the fraction of complexing agents that is complexed by the species absorption,  $P$  is directly related to the species concentration. In practical applications it can be measured eg. by comparing the luminescent light that is coupled in two ridge waveguides having the same donor concentration but with the organic overlayer incorporating the acceptors only coated on one of them.

To demonstrate the performance of a LUQUEN sensor a model system as indicated in fig.8a has been applied. The waveguide consists of a  $\text{Si}_3\text{N}_4$  layer deposited by C.V.D. on a substrate of  $\text{SiO}_2$ . Dye molecules (Rhodamine 6G) incorporated in polyurethane serve as donors. The organic overlayer with chromoionofores (the acceptors) is simulated by Bromocresolpurper (BCP) molecules incorporated in a matrix of polyurethane (10 nm. thickness). The concentration of acceptor molecules and the thickness of the R6G layer are the parameters that can be adjusted. The luminescent spectrum of the R6G molecules is given in fig.9. BCP is a well-known pH indicator (5.2--6.8), hence its spectrum depends on the pH of the environment. Two extreme situations are indicated in fig.9. According to these spectra and (3) the quenching of the R6G luminescence by BCP is pH-dependent. No quenching occurs if  $\text{pH} < 5.2$ , whereas it is "saturated" if  $\text{pH} > 6.8$ . In all our experiments the concentration R6G molecules in the polyurethane film was 0.002 Molar. At this value the donors transfer their energy very fast among each other as confirmed by experiments ( $k_{dd} \gg k_d$ ).

The structure of fig.8a is a detail of the structure of fig.8b. We performed some experiments on the structure indicated. The  $TM_0$  mode of the waveguide is excited with the green light of an Argon laser. The intensity of the luminescent light emitted by the R6G in both the  $TM_0$  and  $TE_0$  modes was measured to be able to calculate the quenching rate  $P_{quench}$ , as a function of the BCP concentration.

This concentration was varied using a 10 nm. thick coating of polyurethane with a carefully adjusted BCP concentration. The luminescent intensity  $I_0$  was measured with the sensor brought into contact with a liquid having a pH=4. In this situation no quenching will occur. Subsequently the pH of the liquid was increased giving an increase in quenching until at pH=8 no further increase could be measured. The intensity of the luminescence in this situation being  $I_1$ .

The measured quenching rate is  $(I_0 - I_1) / I_0$ . The results are indicated in fig.10. Two different thicknesses of the R6G layer have been used (40nm and 400nm). Also indicated is a theoretical fit of the quenching behaviour based on (4) assuming  $f k_{da} = k_d$  at a BCP concentration of 1 Molar. By fitting this curve to the experimental ones a mean value of  $k_{da}$  could be calculated. In an additional experiment the thickness of the BCP layer was varied at a fixed concentration. The response of the sensor did not depend on this parameter when using overlayers thicker than about 5 nm. This result is in agreement with the fact that energy transfer can only occur when donor and acceptor are placed at a very small distance from each other (3).

## 5 Summary and Conclusions.

Solid-state optochemical transducers generally are based on the measurement of the changes in the dielectric function of very thin (organic) overlayers caused by a reversible reaction with the measurand. We have concentrated on organic overlayers having an absorption spectrum that can be modulated as a result of complexation with the species to be measured. In this paper we have demonstrated two different sensing principles that transduce these changes into a variation of an optical signal. The S.P.W. sensor, probing changes in the real part of the dielectric function of the overlayer, is based on linear optics. The output is linearly related to the thickness of the overlayer and the strength of the exploited absorption line. The response time of the sensor is related to the thickness of the overlayer. Given an overlayer of only a few monolayers thickness the principle is only suitable when very strong absorption is combined with a considerable wavelength shift. The example of the cyanine coating that was simulated is about the sensitivity limit of the sensor.

The LUQUEN sensor is based on the modulation of energy transfer in a donor-acceptor system, a non-linear optical phenomenon. The molecules of the overlayer act as a funnel, collecting the energy of a whole assembly of donor molecules. We have shown that using this principle a coverage of the waveguide at the sub-monolayer level is sufficient to easily detect changes in their absorption spectrum.

A necessary condition for this principle to be useful is that the amount of overlap between the acceptor absorption spectrum and the donor emission spectrum is controlled by the concentration of the acceptor complexes and at the same time the spontaneous decay rate of the donor must be low compared with both the donor-acceptor and donor-donor transfer rates. We believe these demands can easily be fulfilled for a wide variety of materials.

Comparing the technological demands that are put to these sensors we can conclude that the S.P.W. sensor is much more complicated than the LUQUEN sensor. Both could also be designed in a fibre geometry. Which for the latter will be more simple.

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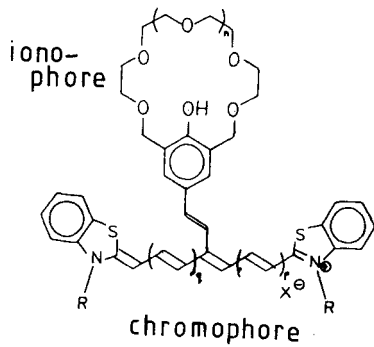


Fig.1 Schematic drawing of the chromoionophore.

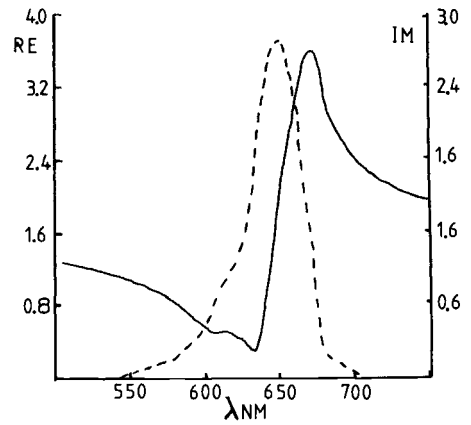


Fig.2 The real part ——— and imaginary part - - - of the refractive index of the chromoionophore.

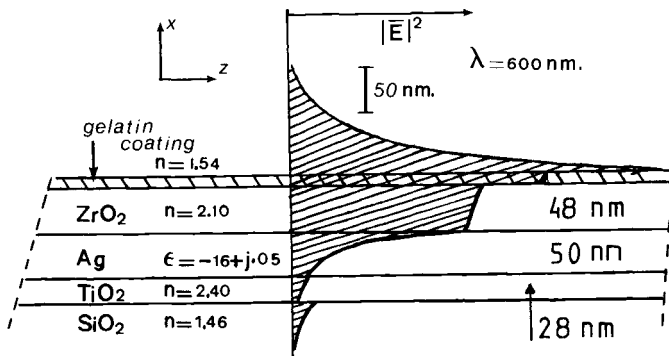


Fig.3 Cross-section of the S.P. guiding section of the multilayered waveguide. Also indicated the distribution of the squared electric field vector.

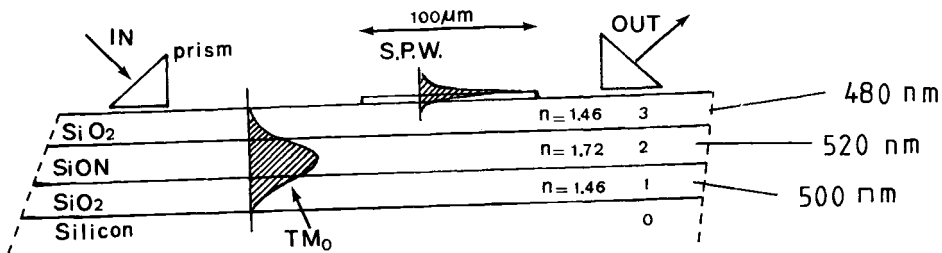


Fig.4 Cross-section of the entire structure.

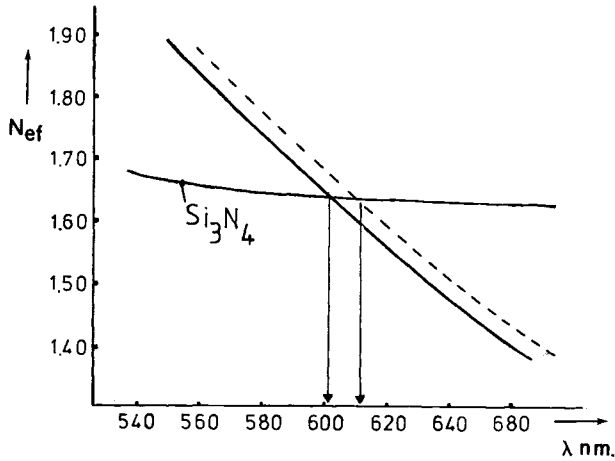


Fig. 5 The dispersion curves of the modes propagating in the S.P.W. sensor.  
 — S.P. mode without gelatine  
 - - - S.P. mode with gelatine

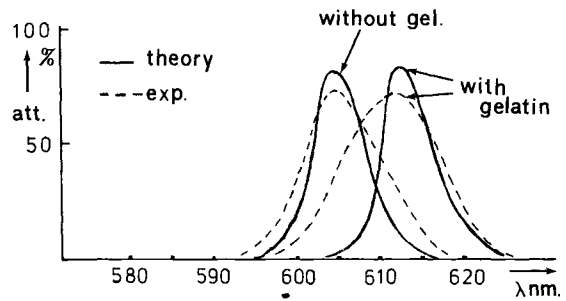


Fig. 6 The filter functions determined with the S.P.W. sensor.

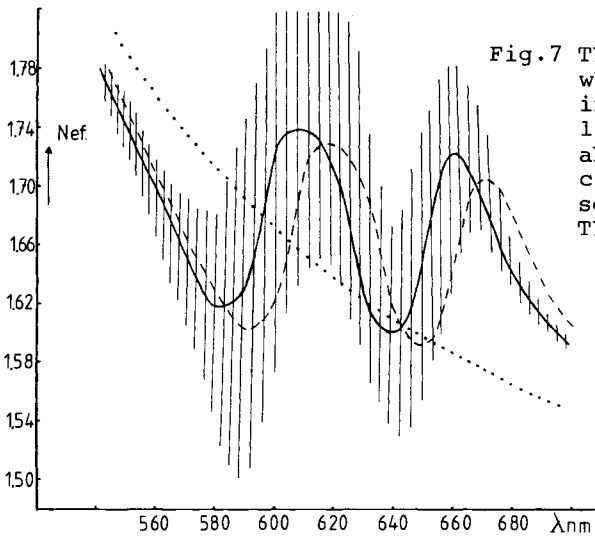


Fig. 7 The dispersion curves of the S.P. mode resulting when a cyanine overlayer is applied. The solid and interrupted curves belong to the same cyanine molecules, the only difference being a shift in their absorption spectrum of 10nm. The shaded area indicates the damping of the mode corresponding to the solid curve. These results are computer simulations.

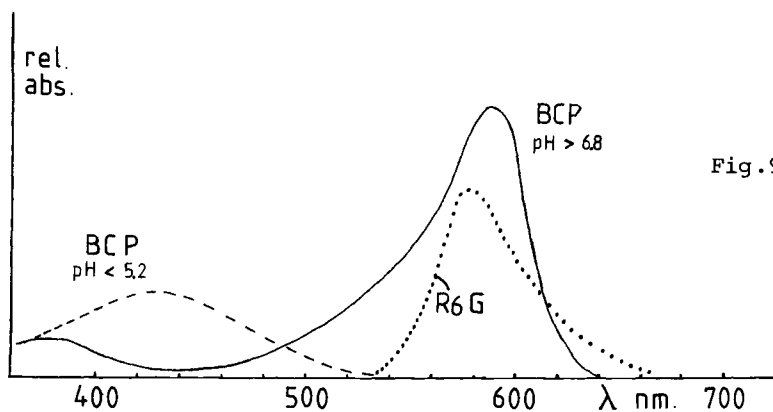


Fig. 9 The absorption spectra of BCP-molecules. Also indicated is the emission spectrum of R6G.

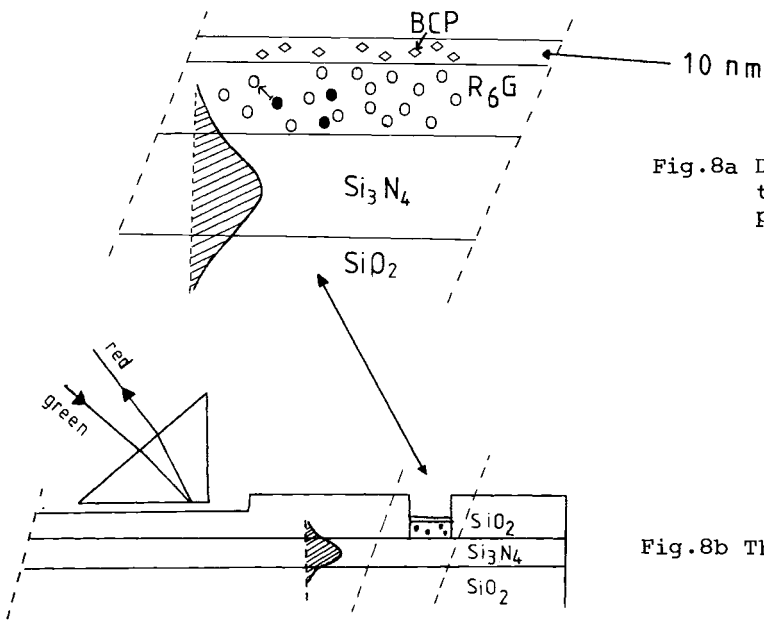


Fig.8a Detail of the LUQUEN sensor indicating the donor and acceptor molecules incorporated in polyurethane.

Fig.8b The entire LUQUEN sensor.

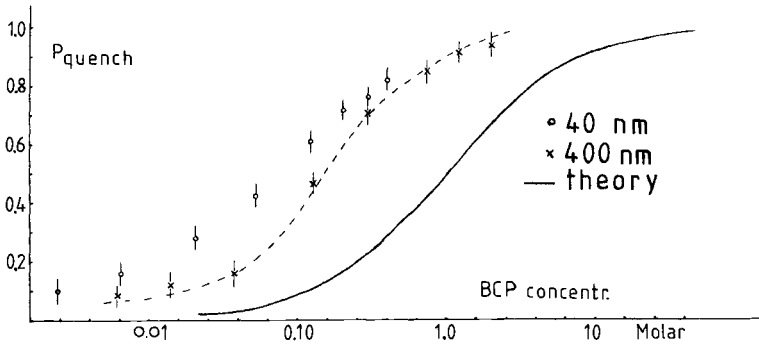


Fig.10 The output of the LUQUEN sensor as a function of acceptor concentration. Experimental data corresponding to two different thicknesses of the R6G layer are given together with a theoretical curve (see text).