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SURFACE PLASMON RESONANCE USING As_2S_3 FILM FOR WATER SALINITY DETERMINATION

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The high sensitivity of chalcogenide surface plasmon resonance (SPR) structures with chalcogenide films is fructified to elaborate the salinity sensor for the seawater. A four layers configuration was taken into consideration, comprising a BK7 prism, a gold thin film, a chalcogenide As_2S_3 film and the ambient medium, which is the sea water. The transfer matrix formalism was used in our study to determine the reflectances characterizing the plasmonic structure. The two polarization modes (TE and TM) were taken into consideration, in order to determine the best configuration that allows an optimal sensitivity.

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1. Introduction

The field of plasmonics have extensively studied over the past decades [1] based on Kreschmann configuration [2]. The concept of four-layer structure that contains gallium lanthanum sulphide amorphous chalcogenide film was proposed in [3], where the resonance was realized by variation of chalcogenide thin film thickness. In [4,5] more particularities of four-layer SPR were highlighted when amorphous, high refractive index films are treated as planar waveguides. The ambient medium was considered air with unit refractive index. In the same time, the most interesting SPR sensors are the biosensors, which measure the refractive index changes in water solutions which have refractive index close to 1.33, which is the index of pure water. Other chemical solutions are of interest, for example water salinity.

A question that rises is why measuring ocean salinity and temperature is important. These two values are closely related to water density and the formation of ocean currents. They also tell us about the exchange of water between the ocean and the atmosphere as part of the water cycle. Some properties of water are changed by having salt in it: salt makes seawater denser than freshwater and salty water needs to be colder than freshwater before it freezes. In this study SPR resonance is proposed as chemical sensor which can determine the seawater salinity with high sensitivity. Specific characteristics of the light interaction with plasmon-polariton waves are done.

2. Water salinity

The refractive index of the sea water depends on three parameters: wavelength, temperature and salinity.

The variation of the refractive index of the distilled water at 25 °C depending on the wavelength is given in [6]. With these values, a value for the considered wavelength (1550 nm) can be easily determined by linear interpolation (there is a very good linearity in the range of 1500 – 1600 nm). Due to the linearity, the next equation can be used to determine the refractive index for a given wavelength: $n = 1.349 - 0.00002 \cdot \lambda$.

The influence of temperature on the refractive index can be deduced from the following experimental data [7]. We took into account 11 wavelengths (between 404.7 and 700 nm) and 7

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temperatures (between 1 and 30 °C) and determined the differences between the refractive index at a given temperature and that at 25 °C. The results are summarized in Table 1.

Table 1. Simulation parameters

λ [nm]	T [°C]						
	1	**5**	**10**	**15**	**20**	**25**	**30**
404.7	0.00151	0.00144	0.00124	0.00092	0.00050	0	-0.00058
435.8	0.00150	0.00143	0.00123	0.00091	0.00050	0	-0.00058
467.8	0.00149	0.00142	0.00122	0.00090	0.00049	0	-0.00058
480.0	0.00149	0.00142	0.00122	0.00091	0.00050	0	-0.00057
508.5	0.00147	0.00140	0.00120	0.00090	0.00049	0	-0.00057
546.1	0.00146	0.00139	0.00120	0.00089	0.00049	0	-0.00057
577.0	0.00145	0.00139	0.00119	0.00089	0.00049	0	-0.00056
579.1	0.00145	0.00139	0.00120	0.00089	0.00049	0	-0.00056
589.3	0.00145	0.00138	0.00119	0.00089	0.00049	0	-0.00056
643.8	0.00143	0.00136	0.00117	0.00088	0.00048	0	-0.00056
700.0	0.00141	0.00135	0.00116	0.00087	0.00048	0	-0.00055
404.7	0.00151	0.00144	0.00124	0.00092	0.00050	0	-0.00058

It can be remarked that, for a certain temperature, the variation of the refractive index with the wavelength is very small (the relative standard deviation is in the range of 1.4 % - 2.1 %). This means that we can consider that the difference between refractive indices at a certain temperature and those at 25 °C is the same for any wavelength. The data thus obtained (centralized in Table 2) suggest a quadratic law: $n(\lambda,T) = n(\lambda,25) - 1.5\cdot 10^{-6}\cdot T^2 - 25\cdot 10^{-6}\cdot T + 15.625\cdot 10^{-4}$, where T is the temperature in °C, λ is the wavelength in nm, n (λ, 25) is the refractive index at wavelength λ and temperature 25 °C, and n (λ, T) is the refractive index at wavelength λ and temperature T.

Table 2. Variation of refractive index with temperature

T [°C]	n (λ,T)- n (λ,25)
1	0.00146
5	0.00140
10	0.00120
15	0.00090
20	0.00049
25	0.00000
30	-0.00057

The influence of salinity on the refractive index can be deduced from the following data found in [8] (which cites [9]) and presented in Table 3.

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Table 3. Refractive index difference vs salinity.

Salinity [‰]	Refractive index difference
5	0.00097
10	0.00194
15	0.00290
20	0.00386
25	0.00482
30	0.00577
35	0.00673
40	0.00769

These data were fitted with a polynomial of 5th order (with coefficients $1.127724\cdot10^{-26}$, $5.128205\cdot10^{-11}$, $-2.284382\cdot10^{-9}$, $-4.603729\cdot10^{-8}$, 0.000194472, and $-1.398601\cdot10^{-7}$).

In our study the refractive indices were determined for five salinity values: 0 ‰ (distilled water), 10 ‰, 20 ‰, 30 ‰ and 40 ‰, at wavelength 1550 nm and temperature 20 °C. Fig. 1 presents the variation of the seawater refractive index with salinity and temperature, at wavelength 1550 nm.

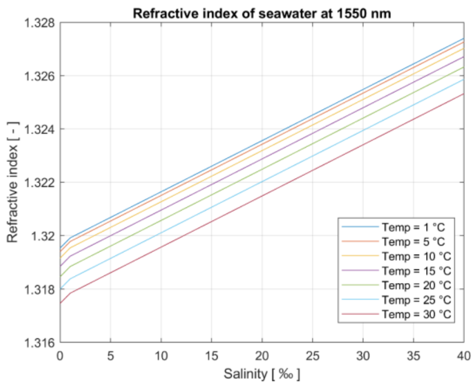

Fig. 1. Refractive index of seawater vs salinity, at different temperatures.

3. Results and discussion

A four layers configuration was taken into consideration, comprising a BK7 prism, a gold thin film, a chalcogenide As_2S_3 film and the ambient medium, which is the sea water, having five different salinities. The layers are described in the Table 4.

Table 4. Layers characteristics

Layer no.	Material	Refractive index	Thickness
1	BK 7	1.500652	-
2	Au	0.559 + i· 9.81	40 nm
3	As_2S_3	2.222680	900 nm
4	Sea water salinity 0 ‰	1.318463	-
	Sea water salinity 10 ‰	1.320572	
	Sea water salinity 20 ‰	1.322491	
	Sea water salinity 30 ‰	1.324409	
	Sea water salinity 40 ‰	1.326327	

In a first stage the propagation constant is calculated [10] for a wide range of As_2S_3 film thicknesses (0 to 6000 nm). The aim of this stage is to determine the optimal As_2S_3 film thickness to get the lowest reflectance minimum and the narrowest notch. Real and imaginary propagation constant β/k variation with As_2S_3 thickness d is shown in Fig. 2.

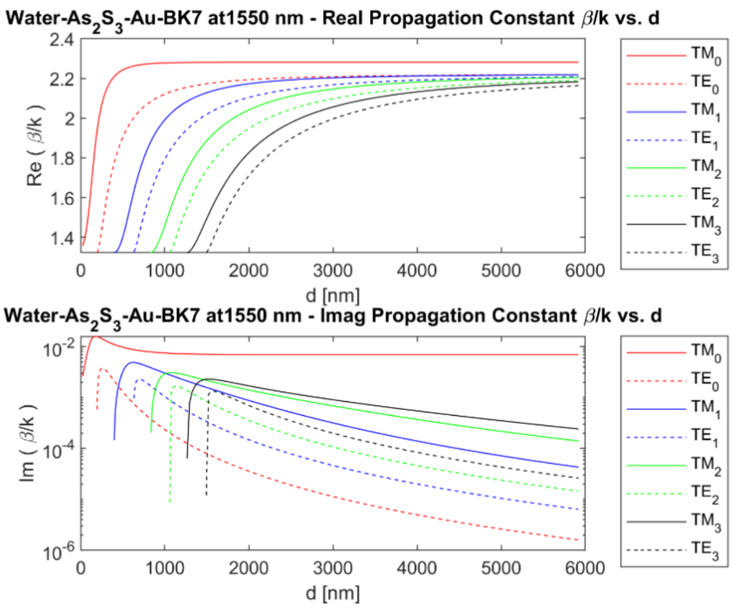

Fig. 2. Real (up) and imaginary (down) propagation constant β/k vs As_2S_3 thickness d.

The thickness of the gold layer was chosen to be 40 nm, a value that allows to get a low reflectance minimum. Basing on the results shown in Fig. 2, the thickness of As_2S_3 layer was chosen to be 900 nm, corresponding to the TM_2 mode.

In the second stage, the transfer matrix formalism was used in our study to determine the reflectances characterizing the plasmonic structure [11].

Five structures (described in Table 1), corresponding to the five salinities taken into account (0, 10, 20, 30 and 40 ‰), were analysed at the wavelength 1550 nm using a very fine mesh of incidence angles, in the range 10° - 80°, with a step of 0.005°. The two polarization modes (TE and TM) will be taken into consideration, in order to determine the best configuration that allows an optimal sensitivity. The simulation parameters are summarized in Table 5.

Table 5. Simulation parameters

Parameter	**Value**
Wavelength	1550 nm
No. of layers	4
Starting angle	10 °
Ending angle	80 °
Angle step	0.005 °

Five structures (described in Table 4), corresponding to the five salinities taken into account (0, 10, 20, 30 and 40 ‰), were analysed at the wavelength 1550 nm using a very fine mesh of incidence angles, in the range 10° - 80°, with a step of 0.005°.

A first result of the simulation is the plasmonic resonance incidence angle dependence of the thickness *d* of the As_2S_3 layer (Fig. 3). For TM_2 and d = 900 nm a plasmonic resonance incidence angle of about 65° is obtained, a value that is very convenient from a practical point of view.

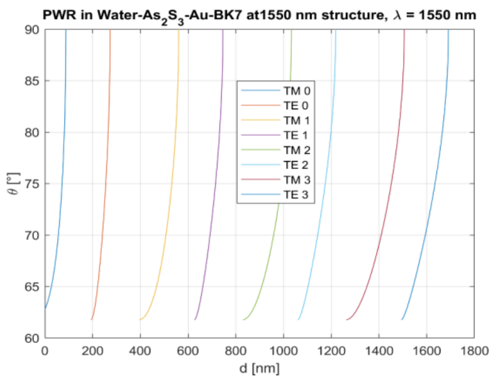

Fig. 3. PWR θ vs As_2S_3 thickness d at 1550 nm for different TM and TE modes.

Then a plot of reflectance dependence on incidence angle at different salinities of the sea water was obtained. Fig. 4 displays only the area of interest (around the plasmonic resonance), i.e. for incidence angles between 60° and 70°.

The results are summarized in Table 6.

Table 6. Plasmonic resonance reflectance and incident angle at different salinities.

Salinity [‰]	R min [%]	θ [°]
0	2.03	64.325
10	1.97	64.460
20	1.92	64.585
30	1.87	64.705

40	1.81	64.830

Plasmonic resonance was reached since very low reflectances (less than 2 %) were obtained. Fig. 5 details the dependence of plasmonic resonance incident angle with salinity.

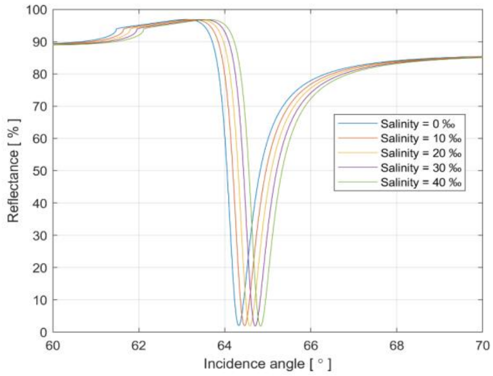

Fig. 4. Reflectance vs. incidence angle at different salinities of the sea water.

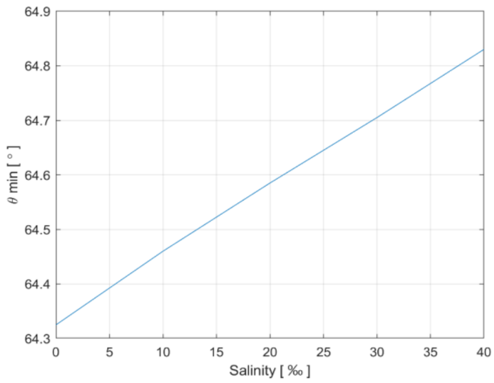

Fig. 5. Plasmonic resonance incidence angle vs. salinity.

It can be noticed the sensitivity: a 1 ‰ change in salinity causes a 45 arc seconds change in plasmonic resonance incident angle. A typical rotation stage with stepper motor has 409,600 microsteps per revolution, which is about 3 arc seconds per microstep. The resulting sensitivity is then 0.07 ‰.

4. Conclusions

A chalcogenide surface plasmon resonance structure was used to accurately determine the salinity of the seawater. The refractive index of seawater dependence on wavelength, temperature and salinity was modelled in order to provide accurate input data for surface plasmon resonance structure design.

A four layers configuration was taken into consideration, comprising a BK7 prism, a 40 nm gold thin film, a 900 nm chalcogenide As_2S_3 film and the sea water as ambient medium.

The plasmon resonance structure was designed in two steps. In a first step propagation constants were calculated for a large range of As_2S_3 film thicknesses and an optimal value (900 nm) for this thickness was found. Thus the lowest reflectance minimum and the narrowest notch were obtained. In the second stage, the transfer matrix formalism was applied to determine the reflectances characterizing the plasmonic structure. The large range of incidence angles (from 10° to 80°, by a very fine step – 0.005°) makes the analysis very accurate.

Plasmonic resonance reflectance and plasmonic resonance incident angle were determined for some salinities of the seawater, resulting a very good sensitivity. The linearity of the plasmonic resonance incident angle dependence on salinity is good enough to allow an interpolation for other salinity values. Plasmonic resonance reflectance was found to be around 2 %.

Better results may be obtained by refining the As_2S_3 film thickness, possibly and gold film thickness.

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