Chalcogenide Letters Vol. 18, No.9, September 2021, p. 535 - 540

Hydrocarbons detection using surface plasmon resonance with As_2S_3 thin film waveguide

L. Baschir[a], S. Miclos[a], D. Savastru[a], I. D. Simandan[b], A. A. Popescu[a*]
[a]*National Institute R&D of Optoelectronics, INOE 2000, 409 Atomistilor str., PO BOX MG. 5, 77125 Magurele, Ilfov, Romania*
[b]*National Institute of Materials Physics, Atomistilor 405A, Magurele 077125, Romania*

Surface plasmon resonance containing amorphous As_2S_3 film is proposed as a chemical sensor to highlight several liquid hydrocarbons. Method is label-free and is based on detection of small changes in the refractive index. As_2S_3 operates as plasmonic waveguide which confines the probing beam to the interface with liquid hydrocarbons. The method can easily distinguish hydrocarbons with very close refractive indices. The film thicknesses were optimized to obtain the best sensitivity and resolving power. Minimum reflectance of SPR less than 1 % was found for optimal calculated film thicknesses, the sensitivity to the refractive index changes being $2 \cdot 10^{-5}$.

(Received March 15, 2021; Accepted September 14, 2021)

Keywords: Chalcogenide Amorphous Materials, Photonics, Plasmonics, Hydrocarbons Detection

1. Introduction

Hydrocarbons are chemical compounds that consist entirely of carbon and hydrogen. These substances are found everywhere given that they participate in the life cycle of living matter, in multiple technological processes, as fuels, and so on. Lighter fractions, such as methane, propane, butane, are in a gaseous state. Others with average molecular weight such as octane are in liquid state. Fractions with an even higher molecular mass are found in solid state and constitute various lubricants, fats.

Over times, several methods of quantitative or qualitative detection and determination of hydrocarbons have been developed. Chemical methods are widely implemented which rely, in particular, on chromatography [1,2]. They have a good accuracy, but require manual preparation of specimens and are difficult to integrate into real time systems or remote sensing of these substances. Optical methods are real-time and can be easy integrated into autonomous systems. They are based on the measurement of spectral optical transmission [3] or reflection [4]. Determining the refractive index has the advantage that it is label-free and therefore more universal. High refractive index sensing can be achieved with plasmonic-based schemes [5]. The phenomenon of surface plasmonic resonance found a practical development after Kretschmann [6] proposed the method of evanescent wave for the coupling of light with the plasmon-polariton wave, confined on the metal-dielectric interface. Several companies sell for some time measurement photonic systems, based on surface plasmon resonance (SPR).

The existence of a sharp resonance caused the increased sensitivity of the sensors based on this principle. The Kretschmann method was developed by us for four-layer structures. Various aspects of this configuration have been studied in [7-12]. In the proposed structure, a film of material with a high refractive index that acts as a wave guide is additionally used. Coupling with waveguide modes has some interesting peculiarities such as the use of low-index prisms such as BK7 glass or adjusting the degree of confining of the electromagnetic field. Amorphous chalcogenide compounds meet this requirement, but also have the advantage that they can be applied on large surfaces and various substrates by well-known vacuum techniques. In this paper we analyzed a concept of optical sensor based on SPR with chalcogenide film made of As2S3 for the determination of hydrocarbons found in liquid state. The study was focused on calculation of

[*] Corresponding author: apopescu@inoe.ro
https://doi.org/10.15251/CL.2021.189.535

resonance curves and optimization the thicknesses of the constituent layers so that, finally, the optimal structure for distinguishing these substances was determined.

2. Surface plasmon resonance hydrocarbon detection

The typical plasmonic planar waveguide consists of a structure of long and large layers in a plane perpendicular to interfaces. In each region the refractive index may be considered constant. The constituent regions are as follows: a substrate made from glass (BK7) which may be considered semi-infinite; a metallic film which have the complex refractive index; a dielectric film made of amorphous chalcogenide which represents the waveguide; a cover region considered semi-infinite (liquid).

Fig. 1 presents schematically the concept of a hydrocarbon detector based on SPR using As_2S_3 film. The hydrocarbon to be tested is admitted through an inlet nozzle in a sealed enclosure that ensures the contact of the hydrocarbon with the BK7 prism hypotenuse, on which the two layers (gold and As_2S_3) are deposited and then is exhausted through an outlet nozzle.

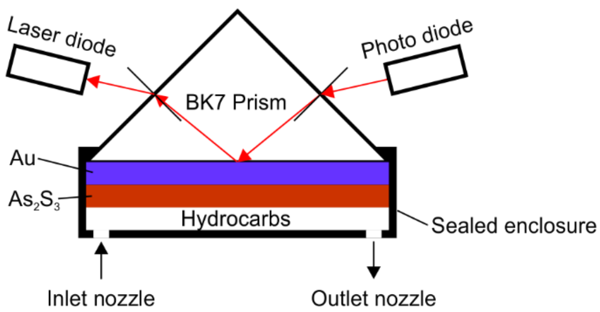

Fig. 1. Hydrocarbons detector schematic concept.

A wavelength of 1064 nm was chosen for this study, one of the 21 wavelengths from our laser diodes library that covers a range between 405 and 1625 nm.

Fig. 2 displays the refractive index variation with wavelengths ranging from 405 to 1625 nm, for benzene and four other hydrocarbons (octane, heptane, pentane and hexane).

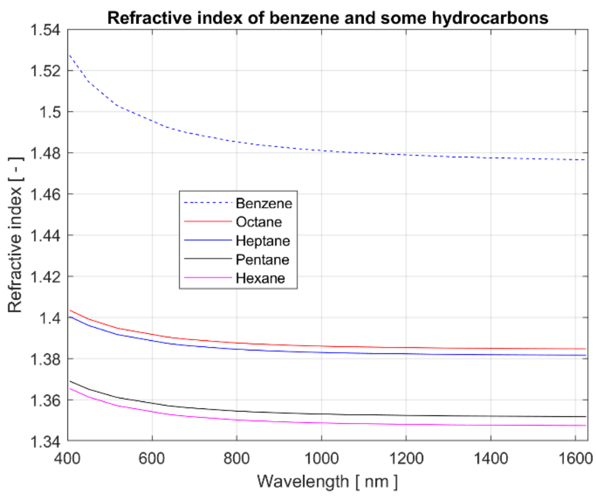

Fig. 2. Refractive index of benzene and some hydrocarbons.

The refractive indices of BK7 were calculated using a dispersion formula [13], those of gold were interpolated from [14]. Refractive indices were calculated using a dispersion formula for As_2S_3 [15], benzene [16], octane, heptane, pentane and hexane [17].

3. Results and discussion

The study considered a four-layer configuration made up of a BK7 prism, a gold thin film, a chalcogenide As_2S_3 film and the ambient medium, which is the analyzed hydrocarbon, as described in the Table 1. Refractive indices are given for the wavelength of 1064 nm.

Table 1. Layers characteristics

Layer no.	Material	Refractive index	Thickness
1	BK 7	1.506635	-
2	Au	0.314837 + 6.628261i	45 nm
3	As_2S_3	2.469346	1220 nm
4	Benzene	1.480182	-
	Octane	1.385795	
	Heptane	1.382728	
	Pentane	1.352854	
	Hexane	1.348514	

Several thicknesses were tried for the gold film, best results (i.e. that allows to get a low reflectance minimum) were obtained for 45 nm. Reflectance curves characterizing the plasmonic structure were calculated using the transfer matrix formalism [6-9, 18-19]. It was sought to obtain an optimum plasmonic resonance (with minimum reflectances under 1 %) by varying the thickness of the As_2S_3 layer. This optimum was found at a thickness of 1220 nm, for all five substances considered as layer 4.

The five structures (described in Table 1) were analyzed at the wavelength 1064 nm using a very fine mesh of incidence angles, in the range 10° - 85°, with a step of 0.005°. The two polarization modes (TE and TM) were taken into consideration, in order to determine the best configuration that allows an optimal sensitivity. The simulation parameters are given in Table 2.

Table 2. Simulation parameters

Parameter	Value
Wavelength	1064 nm
No. of layers	4
Starting angle	10 °
Ending angle	85 °
Angle step	0.005 °

Plasmonic resonance reflectance R_{min} (minimum reflectance), incidence angle θ_{min} and half-measure full width w_{min} are all summarized in Table 3.

The results obtained for plasmonic resonance reflectance R_{min} are very good: 0.43 % (with a width of 0.62 °) for benzene and 0.01-0.02 % (with a width of 0.89 °) for hydrocarbons, proving that plasmonic resonance was reached.

The reflectance dependence on incidence angle is shown in Fig. 3.

Table 3. Plasmonic resonance reflectance, incident angle and half-measure full width

Hydrocarb	R_{min} [%]	θ_{min} [°]	w_{min} [°]
Benzene	0.4256	79.880	0.620
Octane	0.0091	71.225	0.880
Heptane	0.0079	71.050	0.880
Pentane	0.0154	69.455	0.890
Hexane	0.0248	69.245	0.890

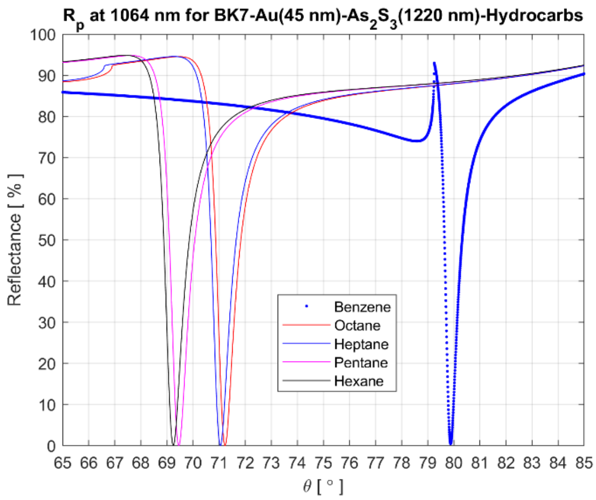

Fig. 3. Reflectance vs. incidence angle for benzene and some hydrocarbons.

Fig. 4 details the dependence of plasmonic resonance incident angle with the refractive index of the analyzed substances.

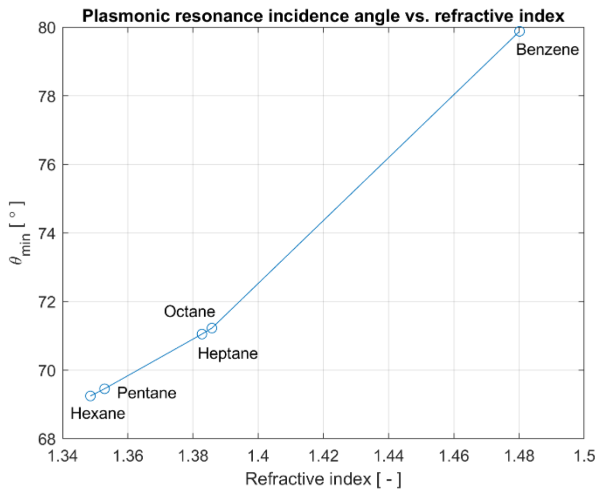

Fig. 4. Plasmonic resonance incidence angle vs. refractive index.

The sensitivity of the surface plasmonic resonance sensor can be calculated as: $= \frac{\Delta n \cdot k}{\Delta \theta_{min}}$, where Δn is the difference between the refractive indices of two successive substances, $\Delta\theta_{min}$ is the corresponding plasmonic resonance incidence angles and k is a transformation factor from degrees to microsteps and equals $k = \frac{360°}{409600}$. The explanation for this factor is that the minimum resolvable angle difference is 1 microstep of the stepper motor of the used rotation stage. For a typical rotation stage there are 409,600 microsteps per 360°. The results were summarized in Table 4.

Table 4. The sensitivity of the plasmonic resonance sensor

Hydrocarb	n [-]	θ_{min} [°]	S [-]
Benzene	1.480182	79.880	0.00000958
Octane	1.385795	71.225	0.00001540
Heptane	1.382728	71.050	0.00001646
Pentane	1.352854	69.455	0.00001816
Hexane	1.348514	69.245	-

Calculated sensitivity is very good: minimum resolvable differences of the refractive index lay in the range 0.000010 – 0.000018, this proving a high sensitivity.

4. Conclusions

The results of this study prove that a chalcogenide surface plasmon resonance structure which contains thin amorphous As_2S_3 film can be used to discriminate between hydrocarbons with very close refractive indices and to determine the concentration of different hydrocarbons in a mixture of components, due to the high sensitivity of the sensor.

The calculations based on a four-layer configuration made up of a BK7 prism, a gold thin film, a chalcogenide As_2S_3 film and the hydrocarbons in the liquid state as ambient medium. The gold and As_2S_3 film thicknesses were optimized during simulation process in order to obtain the best sensitivity and resolving power. The optimal thickness of Au film was found to be 45 nm and that of As_2S_3 film was found to be 1220 nm.

The surface plasmon resonance structure was optimized in two steps. First a large range of As_2S_3 film thicknesses have been tried only for benzene until an optimal value (1220 nm) for this thickness was found, obtaining the lowest reflectance minimum and the narrowest resonance shape. In the second stage the reflectance characterizing the surface plasmonic structure for all studied substances was determined, using the transfer matrix formalism, preserving the As_2S_3 film thicknesses previously found as optimal (1220 nm). The analysis is very accurate due to the large number of incidence angles studied (15000).

Surface plasmonic resonance was obtained, the minimum reflectance being 0.43 % for benzene and 0.01-0.02 % for the other studied hydrocarbons. The refractive index sensitivity was found to be better than 0.00002.

Acknowledgements

This work was supported by the Romanian National Authority for Scientific Research CCCDI-UEFISCDI, through Core Program - project PN 18 N/2019, project PN-III-P2-2.1-PED-2019-4962 within PNCDI III and project number COFUND-ERANET MANUNET III-SensAssist-1, within PNCDI III.

References

[1] W. Moreda, M.C. Pérez-Camino, A. Cert, J. Chromatogr. A., **936,** Issues 1–2, 159, (2001)

[2] R. P. McCue, J. E. Walsh, F. Walsh, Sens. Actuators B Chem., **114,** Issue 1, 438 (2006).

[3] A. Grosch, V. Beushausen, H. Wackerbarth, O.Thiele, T. Berg, R. Grzeszik, J. Quant. Spectrosc. Radiat. Transf., **112**, Issue 6, 994 (2011).

[4] Magnus Wettle, Paul J. Daniel, Graham A. Logan, Medhavy Thankappan, Remote Sens. Environ., **113**, 2000 (2009).

[5] Jeong H. H. et al., Nat. Commun. **7**, 11331, https://doi.org/10.1038/ncomms11331 (2016).

[6] E. Kretschmann, H. Z. Raether, Naturforschung A, 23, 2135 (1968).

[7] A. A. Popescu, R. Savastru, D. Savastru, S. Miclos, Dig. J. Nanomater. Bios., **6** (3), 1245 (2011).

[8] A. A. Popescu, L. Baschir, D. Savastru et al., Rom. Rep. Phys., **67** (4), 1421 (2015).

[9] G. C. Vasile, A. A. Popescu, M. Stafe, S. A. Koziukhin, D. Savastru et al., U.P.B. Sci. Bull. Series A, **75** (4), 311, (2013).

[10] A. Moldovan, M. Enachescu, A.A. Popescu et al., U.P.B. Sci. Bull. Series A., **76** (2), 215 (2014).

[11] I. Lancranjan, D. Savastru, S. Miclos, A. Popescu, J. Optoelectron. Adv. Mater., **12** (12), 2456 (2010).

[12] A. Popescu, S. Miclos, D. Savastru, R. Savastru, M. Ciobanu, M. Popescu, A. Lőrinczi, F. Sava, A. Velea, F. Jipa , M. Zamfirescu, J. Optoelectron. Adv. Mater., **11** (11), 1874 (2009).

[13] https://refractiveindex.info/download/data/2017/schott_2017-01-20.pdf.

[14] Edward D. Palik, Editor “Hanbook of Optical Constants of Solids”, Academic Press 1985.

[15] W. S. Rodney, I. H. Malitson, T. A. King, J. Opt. Soc. Am., **48**, 633 (1958).

[16] K. Moutzouris, M. Papamichael, S. C. Betsis, I. Stavrakas, G. Hloupis, D. Triantis, Appl. Phys. B, **116**, 617 (2013).

[17] K. Kerl, H. Varchmin, J. Mol. Struct., **349**, 257 (1995).

[18] L. Baschir, A. A. Popescu, D. Savastru, S. Miclos, Chalcogenide Lett., **14** (8), 297 (2017).

[19] M. Popescu, D. Savastru, A.A. Popescu et al., Optoelectron. Adv. Mat., **3** (9), 851 (2009).