

## OPTICAL REFLECTION OF $\text{As}_2\text{Se}_3$ -Au PLASMONIC PLANAR STRUCTURE FOR CHEMICAL SENSORS APPLICATIONS

Aurelian A. POPESCU<sup>1c</sup>, Dan SAVASTRU<sup>1</sup>, Mihai STAFE<sup>2c</sup>, Sorin MICLOS<sup>1</sup>,  
Laurentiu BASCHIR<sup>1</sup>, Niculae N. PUSCAS<sup>2</sup>

*Surface plasmon resonance in Kretschmann configuration is studied for a multilayer configuration containing an amorphous chalcogenide film of  $\text{As}_2\text{Se}_3$ . We investigated numerically and experimentally the resonance curve of a four-layers plasmonic structure. The  $\text{As}_2\text{Se}_3$  film of the structure was deposited by vacuum thermal deposition over thin bare gold film. It was shown that for some amorphous film thicknesses the coupling between light beam and surface plasmon wave could be achieved by use of low refractive index prism like BK7 glass. The improved sensitivity of multilayers structure to small variations of the ambient refractive index as compared to the three layers Kretschmann configuration is highlighted.*

**Keywords:** plasmonics, surface plasmon resonance, amorphous chalcogenide materials, photonics, vacuum film deposition.

### 1. Introduction

At the metal-dielectric interface, at certain irradiation conditions, surface plasmon-polariton waves can be formed. Based on this phenomenon, a large range of photonic devices were proposed. The plasmon-polariton waves can be excited in a structure consisting of a metallic film (usually gold, which has lower optical losses) deposited on a prism base. With near 50 nm metallic film thicknesses, the plasmon-polariton wave is excited by the light that propagates in the prism under a specific angle named surface plasmon resonance (SPR) angle, so that the intensity of the reflected light is close to zero. It was demonstrated that the SPR angle value is very sensitive to small variations of the refractive index of ambient medium and the reflectivity curve was proven to be very narrow. In this way, a high sensibility to variation of the refractive index of the ambient medium was obtained. This led to the development of label-free chemical sensors with high sensitivity.

The subject is several decades old, after Kretschmann proposed a prism method which uses attenuated total reflection for coupling of the light into the surface plasmon [1]. This phenomenon was used for the development of plasmonic

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<sup>1</sup> National Institute of R&D for Optoelectronics INOE 2000, Magurele, Ilfov, Romania

<sup>2</sup> University "POLITEHNICA" of Bucharest, Department of Physics, Bucharest, Romania

c Corresponding authors: mihai.stafe@physics.pub.ro; apopescu@inoe.ro

sensors [2-4]. The results were particularly impressive in the case of biological selective sensors [5-7]. The irradiation by light enhance photodarkening in amorphous chalcogenide materials [8] due to localized plasmons in the presence of gold nano particles. Chalcogenide glasses are promising media for active plasmonic devices [9-11]. The sensor detection limit for refractive index was less than  $10^{-5}$ .

One of the first plasmonic sensors realizes gas detection [12]. The surface plasmon resonance (SPR) biosensors were especially successful when were used for study of biomolecular interactions in real time. The plasmonic sensors technology was commercialized by several companies such as BIACORE (Sweden), Texas Instrument (USA), Xantec (Germany). Different authors [13-15] investigated the sensitivity of SPR sensors to the refractive index changes.

The plasmonic chemical sensors feasibility by using multi- layer planar structure are studied in this paper. The structure contains an  $\text{As}_2\text{Se}_3$  amorphous chalcogenide film with high refractive index of 2.8 forming planar plasmonic waveguide. The coupling conditions of IR light with waveguide modes are analyzed.

## **2. SPR: Four layers configuration schematic**

Conventional SPR Kretschmann arrangement was analyzed in paper [1]. Our four-layer structure design containing amorphous arsenic sulfide film was described early in our papers [16,17]. The lower ambient medium may be considered semi-infinite. However, the energy is confined near the interface with amorphous chalcogenide film.

The planar four-layer waveguide structures containing arsenic selenide film are characterized by higher refractive index than arsenic sulfide. Small attenuation in the structure occurs due to contact with the gold film which exhibits low attenuation. The semi-infinite layer corresponding to the ambient medium was chosen to be air or water. The incident laser beam undergoes attenuated total internal reflection on the prism base. The evanescent field extends through the thin metal film to its lower surface. At resonance, the velocity of plasmon-polariton wave equalizes the speed of light and a sharp dip appear in the reflected signal due to strong interaction of the plasmonic structure with light.

## **3. SPR in multilayer structures: numerical calculations**

Let us consider that the linearly polarized laser radiation is sent at different incidence angles  $\theta$  on the BK7 prism-gold film- $\text{As}_2\text{Se}_3$  film interfaces so that to excite the TM modes of the waveguide. In this case, it is demonstrated that the whole electromagnetic field within the waveguide can be derived by calculating the normal to the incidence plane component ( $H_y$ ) of the magnetic field in every region

of the plasmonic structure. The propagation equation for  $H_y$  in the four planar layers, characterized by the refractive indexes  $n_1 \div n_4$ , may be written in the form of Helmholtz equations system:

$$\frac{\partial^2 H_y}{\partial x^2} + (k_0^2 n_i^2 - \beta^2) H_y = 0 \quad (1)$$

where  $i=1 \div 4$ ,  $k_0$  is the vacuum wave vector, and  $\beta = k_0 n_1 \sin(\theta)$  represents the propagation constant. Here,  $x$  axis is the in-plane direction perpendicular to the structure layers. The continuity equations for the magnetic and electric fields at the three interfaces of the waveguide structure are applied to complete the system.

The Helmholtz equations (1) have analytical solution only for one metal-dielectric interface. For our four-layers structure (consisting of BK7 coupling- gold film- As<sub>2</sub>Se<sub>3</sub> film- air/water), there are at least three interfaces (prism-metal, metal-As<sub>2</sub>Se<sub>3</sub> film, As<sub>2</sub>Se<sub>3</sub> film-air (or water)). As in our previous papers [16,17] the reflectivity  $R_p$  of the multilayer structure as a function of incidence angle was calculated by using the transfer matrix method, largely applied for multilayer optical thin films design [18].

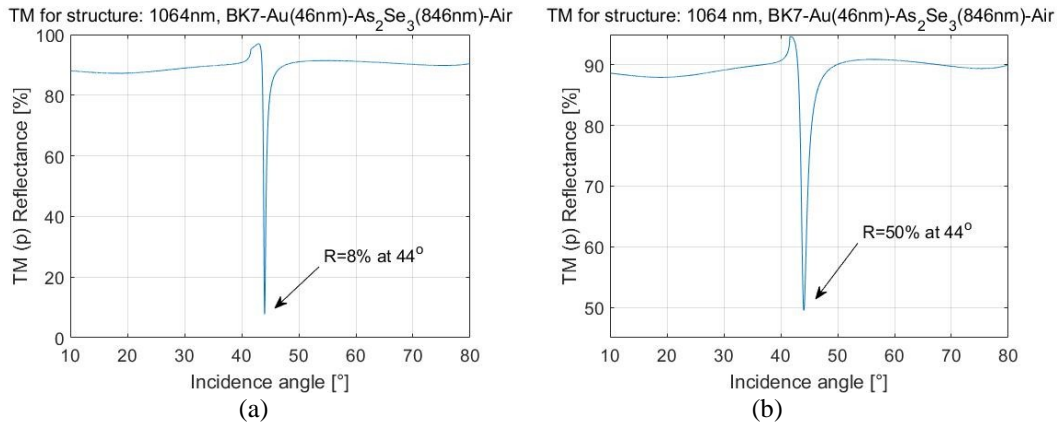


Fig. 1. Resonance curve of the plasmonic structure for two extinction coefficient values:  $k=0$  (a) and  $k=0.01$  (b). As<sub>2</sub>Se<sub>3</sub> layer thickness is 846 nm and Au film thickness is 46 nm in both cases.

In the wavelength domain employed here, the amorphous chalcogenide films exhibit optical absorption. The extinction coefficient and the refractive index of As<sub>2</sub>Se<sub>3</sub> in the plasmonic structure were measured by spectrometric ellipsometry and are the follows: the refractive index of As<sub>2</sub>Se<sub>3</sub> is  $n=2.78$  and its extinction coefficient is  $k=0.01$ . The others input parameters for the calculations are as follows: TM modes,  $\lambda=1064$  nm; complex refractive index of the gold film is  $(0.6827 - i2.0203)$  [19]; the refractive index of BK7 glass  $n=1.5066$  is well known.

The extinction coefficient of As<sub>2</sub>Se<sub>3</sub> ( $k=0.01$ ) corresponds to an absorption coefficient  $\alpha=100$  cm<sup>-1</sup> which, although is small, it led to major changes of the

reflectivity minimum. Figure 1 presents the calculations for the  $\text{As}_2\text{Se}_3$  film considering two different cases: non-absorbing film ((a),  $k=0$ ) and absorbing film ((b),  $k=0.01$ ). The results show that even this small absorption decreases the quality of the SPR structure and leads to an increase of the reflectance up to 50%. For films without absorption, the minimum drops up to 8% and can be even smaller by optimizing the film thickness.

#### 4. SPR setup and experimental results

The SPR experimental setup is presented in Fig. 2. The SPR structure contains a chipset made up of a glass slide covered with gold film. It was used standard chipset from XanTec bio-analytics Company. The gold film thickness was demonstrated to be 46 nm by profilometer measurements.

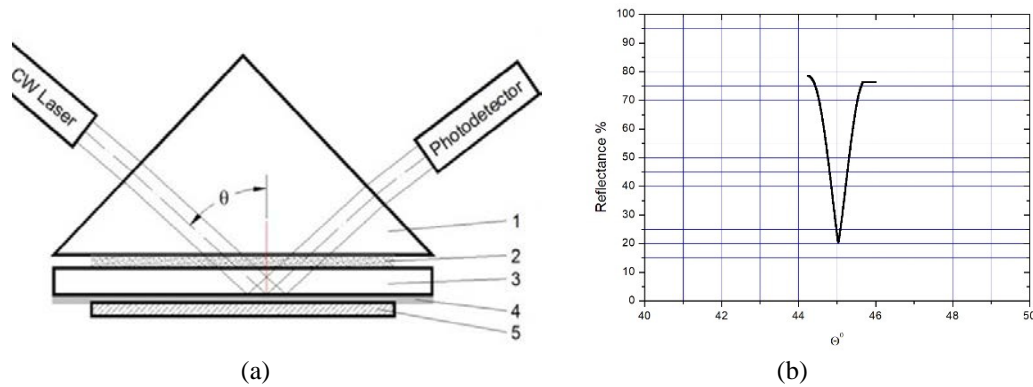


Fig. 2. (a) Experimental setup for the investigation of SPR with amorphous  $\text{As}_2\text{Se}_3$  film: 1-prism of BK7 glass; 2-immersion oil; 3-substrate glass slide; 4-gold film; 5- $\text{As}_2\text{Se}_3$  amorphous film. (b) Experimentally measured reflectance versus incident angle.

The  $\text{As}_2\text{Se}_3$  film was deposited over thin gold film by thermal evaporation and presents a single chipset. The chipset is attached to the base of a right-angle prism by using immersion oil. The arsenic selenide film thickness was of 846 nm and was measured by stylus profilometer. P-polarized light of YAG:Nd acousto-optic Q-switch laser was coupled with TM- mode of planar waveguide formed by  $\text{As}_2\text{Se}_3$  thin film.

The uses of BK7 material for fabrication of coupling prism is very convenient as it is cheap and affordable. The SPR sensitivity as chemical sensors depends on geometry. For the three-layers Kretschmann configuration the results are well known. However, better results can be obtained in four layers SPR configuration. Have a look to the Figure 3 bellow presenting the theoretical reflectivity of the SPR structure obtained for two different chalcogenide film thickness. The reflectivity curves are sharp and very narrow. Large shift ( $\sim 1$  degree)

of resonance curves can be observed in both cases for only 0.01 changes of the ambient refractive index. The sensitivity is competitive with other optical resonance sensors, e.g. LPG fiber optic chemical sensors [20]. Also, one can see from Fig.3b that the position of resonance depends strongly of the amorphous film thickness.

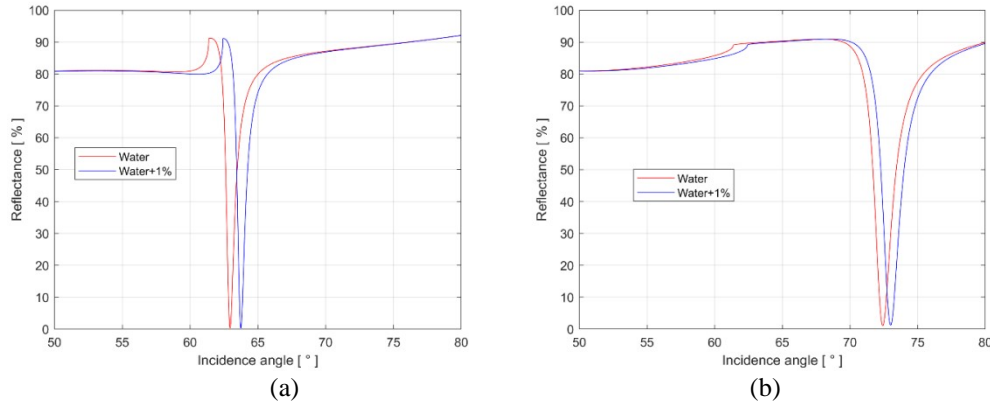


Fig. 3. SPR shape and deep shift when refractive index of ambient changes from 1.33 (pure water) to 1.433 (water solution). The chalcogenide film thickness is 600 nm (a) and 800 nm (b).

## 5. Conclusions

The numerical simulations of SPR for structures containing As<sub>2</sub>Se<sub>3</sub> amorphous film were performed. The calculations demonstrate that SPR waves exist for any thickness of amorphous As<sub>2</sub>Se<sub>3</sub> film, but the light can be coupled with plasmon-polariton mode only for some well-defined amorphous film thicknesses. The narrower minimum and the larger shift of reflectivity occurs in the four layers SPR structure which contains As<sub>2</sub>Se<sub>3</sub> dielectric film with a high 2.8 value of the refractive index. The higher the film refractive index, the stronger is the confinement of light and the sensitivity of structure to the refractive index variation. The sharp resonance minimum was experimentally confirmed for As<sub>2</sub>Se<sub>3</sub> films with thickness of 846 nm. The water solutions present an important case as many processes take place namely in these conditions. We established numerically that the sensibility of the plasmonic chemical sensors to small variations of the refractive index of water is better for this 4-layers configuration as compared to the 3-layers configuration and As<sub>2</sub>S<sub>3</sub> structures.

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