

AMORPHOUS ARSENIC SELENIDE FILMS FOR OPTICAL MEMORY BASED ON SURFACE PLASMON RESONANCE

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We present a theoretical study on the reflectivity of a plasmonic structure based on As_2Se_3 amorphous chalcogenide film as a function of the refractive index of the chalcogenide film. In plasmonic configuration, the thin chalcogenide films constitute an optical waveguide, and we show that for specific thicknesses of the plasmonic structure layers, the reading-laser radiation can excite TM waveguide modes efficiently. Thus, we demonstrate that for chalcogenide film thickness of 700 nm, the resonance coupling-angle is equal to 49.16° at the reading-laser wavelength of 1064 nm. When irradiating the chalcogenide film with a linearly polarized writing-laser at a wavelength in the absorption edge of the chalcogenide, the resonance peak experiences a large shift due to the laser induced variation of the chalcogenide refractive index. This enabled us to demonstrate that by keeping a constant incidence angle of 50.0° , which is slightly above the resonance angle, a sharp peak of the reflectivity at the reading-laser wavelength is observed when increasing the chalcogenide refractive index with $\sim 0.5\%$ by writing-laser irradiation. The results presented here can be used for development of devices with bistability or optical memory.

Keywords: amorphous chalcogenide film; surface plasmon resonance; optical waveguides.

1. Introduction

The non-crystalline chalcogenide compounds constitute a special group with distinct physical properties. The binary and ternary chalcogenide compounds are characterized by a wide vitrification range with variation of the refractive index in the domain 2.2–3.0. One and the same chemical composition constitute materials with different glass network structure due to the reorientation of the valence bond of chalcogen. Under the light irradiation the refractive index and the coefficient of optical absorption are considerably modified. The materials can be

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obtained in the form of thin films of good quality on various substrate. Photoinduced changes in optical parameters (refractive index and optical absorption coefficient) correlate with changes in material structure.

Studies of laser induced effects in chalcogenide glasses were initiated by seminal paper of Tanaka (1976). Mainly two approaches were proposed for explanations: the first emphasized the electronic origin of photodarkening [1, 2] and involve metastability of local structures formed as charge carriers are produced and recombine. The second emphasized structures, mainly layered structures, like in As_2S_3 and As_2Se_3 glasses [3]. The restoration is obtained by subsequent heating which isn't convenient for practical application. Another phenomenon identified by Zhdanov&Malinovski [4] in amorphous chalcogenide (a-ChG) films is the appearance of photo-induced refractive index dichroism, or optical anisotropy, when films are irradiated with polarized light. Although the publication appeared in 1977, no realistic proposal for applications were made till now as the changes of refractive index are quite small, about 10^{-3} . However, the physical effect has a considerable advantage: it is fast, under nanosecond relaxation times. Recently, a compact field-effect plasmonic modulator has been demonstrated [5] and the direct optical modulation on femtosecond timescale has been reported [6]. That is because the inducing of anisotropy involves chemical bond switching only, without the changing of atoms position in space. The switching can be very fast by using higher power and short laser pulses as this phenomenon depends on applied pulse energy.

The amorphous ChG are used for a range of important applications, focusing on recent examples in mid-infrared sensing, integrated optic, ultrahigh-bandwidth signal processing [7, 8]. Also, using the SPR method combined with a ChG films characterized by reversible optical transmission changes it is possible to realize devices having optical memory. Under well-defined conditions [9] that depend on the optical constants of materials, at certain angle the incident light can be coupled with surface plasmon wave. As a result of the interaction, the energy of the light beam is absorbed into the material and the intensity of the reflected light becomes almost null. In the resonant structure such as surface plasmon resonance (SPR) with amorphous chalcogenide thin film small changes of refractive index are greatly amplified.

The changes of structure reflectance are based on angular interrogation in which a prism for the excitation of surface plasmons by light is used [10-12]. The resonance angle changes were obtained by depositing a thin amorphous chalcogenide glass (a-ChG) layer on the substrate surface whose refractive index may be modified by the external irradiation [13]. The authors use a rutile prism which has high refractive index of the GaLaS film, necessary condition for the excitation of surface plasmon. The refractive index of most chalcogenide

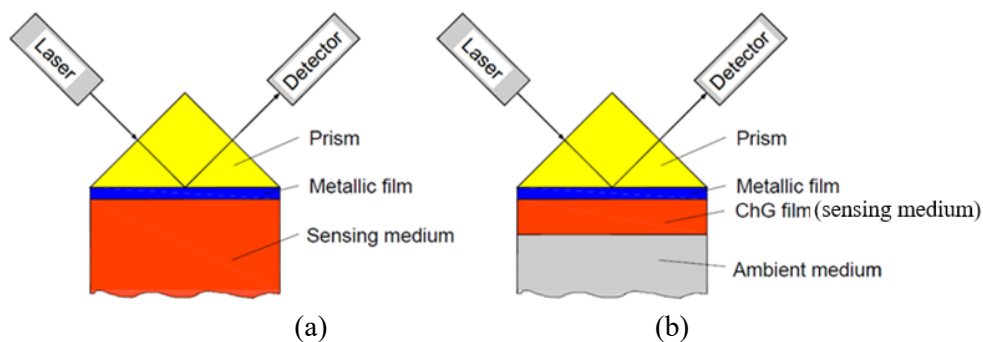
materials is very high, in the range of 2.2-3.0. The use of excitation prism with such high refractive index is inconvenient.

The losses study in planar chalcogenide $\text{As}_x\text{S}_{1-x}$ waveguides done in paper [14] demonstrated that high quality planar waveguides can be obtained. The coupling of light in plasmonic waveguide modes is an appropriate method for structures which contain a-ChG film with high refractive index. Any variation of the refractive index near the metal-dielectric interface determines the shift of the resonance angle. This was used for the development of high sensitivity sensors as the SPR resonance peak is very sharp. The main feature of such SPR configurations we have published yearly in paper [15] and later [16-17] as SPR for sensors.

In this paper we study changes of the SPR reflectivity which occur due to changes of the As_2Se_3 amorphous chalcogenide film refractive index. Such changes can be obtained by irradiating the film with light. The aim of this study is to determine the resonance peaks for different refractive index of the chalcogenide layer. The calculation method and calculated reflectance are presented.

2. Four-layers plasmonic resonance structure

A SPR system set up in the conventional three layers Kretschmann arrangement is done in Fig. 1a. The setup can be used as optical sensor for analyzing the variations of the sensing medium parameters. The four-layers configuration presented in Fig. 1b can be used as optical memory where information is recorded in the chalcogenide film by a writing-laser (in figure is presented only the reading-laser). We analyzed the four layers configuration by numerical simulations.



Figs. 1. Three-layers SPR configuration (a) and (b) four layers-SPR configurations.

Chalcogenide glasses are characterized by high refractive index and thus chalcogenide glasses of finite thickness can form planar waveguide. In the configuration employed an incident beam undergoes total internal reflection at the

prism base, generating an evanescent field that extends through the thin metal film to couple to the plasmon mode on its lower surface. The resonance corresponds to the condition when the phase velocity of light parallel to surface equalizes the velocity of surface plasmonic wave. At the resonance a sharp dip appears in the reflected signal due to strong light absorption by plasmons.

3. Method for calculation of resonance curves

Our physical model for plasmonic structure corresponds to a four-layer optical system (Fig. 1b). For this configuration is not possible to obtain explicit formula for the structure reflectivity.

Calculations formulas for reflectance are derived from the mean square electric fields induced by plane electromagnetic radiation in a two-layer, three-layer, and generally N -layer structure. The first (incident) and last layers are considered semi-infinite. The layers of the structure are considered isotropic with known optical constants, and the boundaries which separate layers are plane and parallel.

Simple relationships can be obtained by deriving the equations for the general N -layer case in terms of characteristic matrices [18]. In this formalism the tangential fields at the first boundary are related to those at the last boundary by the relation:

$$\begin{bmatrix} U_1 \\ V_1 \end{bmatrix} = M_2 \cdot M_3 \cdots M_{N-1} \cdot \begin{bmatrix} U_{N-1} \\ V_{N-1} \end{bmatrix} \quad (1)$$

The matrices M_k have the form

$$M_k = \begin{bmatrix} \cos \beta_k & (-i \sin \beta_k) / q_k \\ (-i \sin \beta_k) q_k & \cos \beta_k \end{bmatrix} \quad (2)$$

where β_k and q_k can be computed as:

$$q_k = \sqrt{\varepsilon_k - (n_1 \cdot \sin \theta_k)^2} \quad (3)$$

$$\beta_k = \frac{2\pi}{\lambda} d_k \sqrt{\varepsilon_k - (n_1 \cdot \sin \theta_k)^2} \quad (4)$$

Here ε_k denotes the complex refractive index; θ_k - ray angle of incidence on k -layer; λ - wavelength of the light.

The calculated reflectivity R_p for the p -polarized light has the form:

$$R_p = \left[\frac{(M_{11} + M_{12}q_N)q_1 - (M_{21} + M_{22}q_N)}{(M_{11} + M_{12}q_N)q_1 + (M_{21} + M_{22}q_N)} \right]^2. \quad (5)$$

SPR computation was realized by using two scripts written in MATLAB: the first script enables calculation of the structure reflectivity as a function of

incidence angle and determination of the resonance angle. The second script enables us to calculate the structure reflectivity as a function of refractive index of the ChG film.

4. Results of SPR calculations

We analyzed the reflectivity of the 4-layer plasmonic structure based on the As_2Se_3 film (see Fig. 1(b)). In the one-dimensional case, for transverse magnetic (TM) modes we evaluated the magnetic field distribution. The magnetic field distribution within a 700 nm thick As_2Se_3 ChG layer as a function of transverse x position, for TM2 mode at 1064 nm wavelength of the reading-laser, is given in Fig. 2.

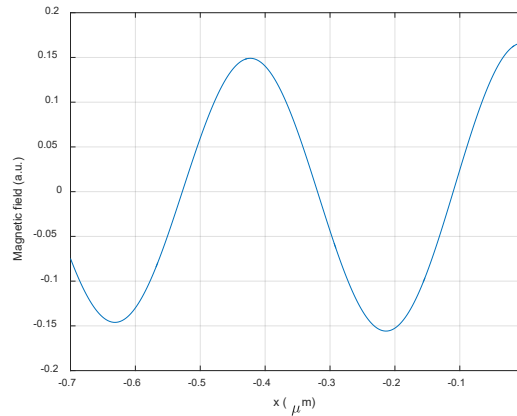


Fig. 2. Magnetic field distribution across the chalcogen film at TM2 propagation mode in the chalcogen layer for a film thickness of 700 nm at 1064 nm wavelength.

The calculation of the reflected field at the prism-metal interface allows the obtaining of resonance curves describing the dependence of the reflectance R on the incidence angle. TM2 (i.e. p -polarized) mode for As_2Se_3 based plasmonic structure were calculated by using the following material and geometrical parameters: semi-infinite BK7 glass with refractive index 1.5066 [19], 46 nm thickness gold layer with complex refractive index $0.2585-i6.9654$ [20], 700nm thickness As_2Se_3 with complex refractive index $2.6786-i0.0033$ [21], and semi-infinite air with refractive index 1. The reading-laser wavelength of 1064 nm was selected in the transparency domain of As_2Se_3 .

The simulations indicate that the optimal thickness of the ChG film is 700 nm for obtaining a resonance curve at an incidence angle which, from a practical point of view, has to be in the $40\div50$ degrees range (Fig. 3). The resonance corresponds to the condition when the phase velocity of light parallel to surface equalizes the velocity of surface plasmonic wave. At the resonance a sharp dip

appears in the reflected signal due to strong resonant absorption by plasmons. Close to resonance angle the resonance curve is very sharp. The minimum reflectance was obtained for the incidence angle of 49.16° .

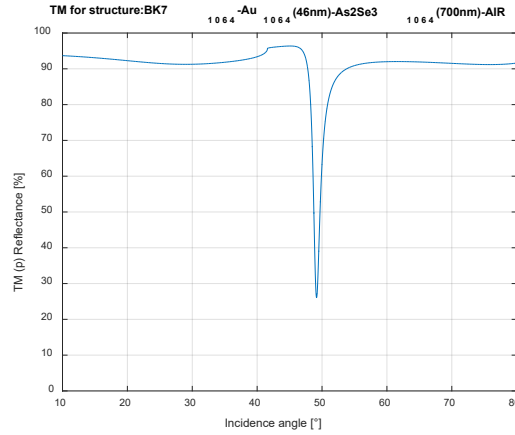


Fig. 3. Reflectivity vs incidence angle for film thickness of 700 nm.

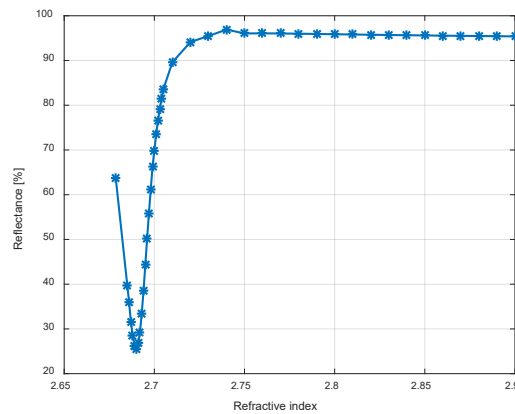


Fig. 4. Reflectance vs As_2Se_3 refractive index.

In Fig. 4 we present the dependence of reflectance as a function of ChG refractive index for TM2 mode for a 50° incidence angle, which is slightly above the of 49.16° resonance angle of the plasmonic structure. In our simulations, the refractive index of the ChG film was varied between 2.66 and 2.90. As can be seen in the Fig. 4, the reflectance reaches a minimum for a value 2.69 of refractive index (which is $\sim 0.5\%$ above the nominal value of 2.6786) and then increases abruptly with the increase of the chalcogenide material refractive index followed by saturation. This behavior can be related to the following phenomenon: the increase of the As_2Se_3 refractive index leads to shift of the resonance deep position (presented in Fig. 3) from 49.16° to 50° .

The variation of the ChG refractive index may be induced by increasing the power of a linearly polarized writing-laser with the wavelength in the absorption edge of the ChG layer (for example 514 nm wavelength from an Ar⁺ laser). We note here that irradiation with unpolarized light does not cause anisotropic changes of the ChG refractive index. The variation of the ChG refractive index enables "optical memory" which manifest in that the reflectance of the structure after „printing" the information with the p-polarized writing-laser retains its value even after irradiation. Subsequent irradiation with orthogonal polarized laser restores the value of the ChG refractive index and the reflectance of the plasmonic structure returns to the original value before irradiation, so erasing the photo-induced state. Therefore, bistable or optical memory devices can be developed when the refractive index is changed by light irradiation.

5. Conclusions

Surface plasmon resonance in Kretschmann configuration was studied theoretically for a multilayer configuration containing the As₂Se₃ amorphous chalcogenide film. For a plasmonic structure comprising a 46 nm gold film and a 700 nm chalcogenide film thickness we obtained a resonance curve and the minimum reflectance of the structure for a 49.16 ° incidence angle of the reading-laser beam at 1064 nm wavelength. The study was performed for the TM₂ transverse magnetic mode of the ChG optical waveguide. The reflectivity of the structure changes is modified as the refractive index of the ChG layer changes. We demonstrated that by setting a constant incidence angle for the reading laser slightly above the resonance angle, the reflectance of the plasmonic structure has a sharp dip for a refractive with ~0.5% above the nominal value of the ChG refractive index. This small variation of the refractive index could be induced by a linearly polarized writing-laser with the wavelength in the absorption edge of the ChG layer (for example 514 nm wavelength from an Ar⁺ laser). The result presented here can be used for the development of devices with bistability or optical memory.

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REFERENCES

- [1] K. Shimakawa, A. Kolobov, S.R. Elliott, Photoinduced effects and metastability in amorphous semiconductors and insulators, *Advances in Physics*, Vol. 44, Issue 6, p. 475-588, 1995.
- [2] Popescu M., Sava F., Lorinczi A., Savastru R., Savastru D., Radvan R., Mihailescu I.N.J., G. Socol, Optical recording in sulfur-selenium layers, *Journal of Optoelectronics and Advanced Materials*, Vol. 6, Issue 3, p. 883-886, 2004.
- [3] K. Shimakawa, N. Yoshida, A. Ganjoo, A. Kuzunawa, J. Singh, *Phil. Mag. Lett.*, Vol. 77, Issue 3, p. 153, 1998.
- [4] V. G. Zhdanov, B. T. Kolomiets, V. M. Lyubin, V. K. Malinovskii, *Photoinduced optical anisotropy in chalcogenide vitreous semiconducting films*, *Phys. status solidi A*, Vol. 52, Issue 2, p. 621, 1979.
- [5] J. A. Dionne, K. Diest, L. A. Sweatlock, and H. A. Atwater, PlasMOSor: a metal-oxide-Si field effect plasmonic modulator, *Nano Lett.*, Vol. 9, Issue 2, p. 897-902, 2009.
- [6] Kevin F. MacDonald and Nikolay I. Zheludev, Active plasmonics: current status, *Laser Photonics Reviews*, Vol. 4, Issue 4, p. 562-567, 2010
- [7] B. J. Eggleton, B. Luther-Davies and K. Richardson, Chalcogenide photonics, *Nat. Photonics*, Vol. 5, p. 141-148, 2011.
- [8] A. Popescu, Components for integrated optics based on amorphous chalcogenide materials *Romanian Report in Physics*, Vol. 51, 3-4, p. 327-330, 1999.
- [9] E. Kretschmann, and H. Raether, Radiative decay of non-radiative surface plasmons excited by light, *Zeitschrift Naturforschung a* 23 (12), pp. 2135-2136, (December 1968).
- [10] A.A. Popescu, R. Savastru, D. Savastru, S. Miclos, *Digest Journal of Nanomaterials and Biostructure*, Application of vitreous As-S-Se chalcogenides as active layer in surface plasmon resonance configuration, Vol. 6, No. 3, p. 1245-1252, 2011.
- [11] H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, Springer, Berlin, Germany, 1988.
- [12] S. A. Maier, *Plasmonics – Fundamentals and Applications*, Springer, New York, 2007.
- [13] Zsolt L. Samson, Shih-Chang Yan, Daniel W. Hewak, and Nikolay Zheludev, *Phys. Status Solidi RRL*, Vol. 14, No. 10, p. 274, 2010.
- [14] Popescu A. A., Savastru D., Miclos S., Design and realization of low losses chalcogenide AsxS1-x planar waveguides, *Journal of Optoelectronics Advanced Materials*, Vol. 13, Issue 2-4, p. 213-217, 2011.
- [15] L. Baschir, S. Miclos, D. Savastru, A. A. Popescu, “E. Coli detection using surface plasmon resonance”, *Chalcogenide Letters*, vol. 18 (6) , pp.283-288, 2021.
- [16] A. A. Popescu, L. Baschir, D. Savastru, M. Stafe, C. Negutu, V. Savu, Georgiana Vasile, Mona Mihailescu, Victor V. Verlan, Olga Bordian, N. N. Puscas, Surface plasmon resonance and photoinduced dichroism in amorphous chalcogenide As₂S₃ films, *Romanian Reports in Physics*, Vol. 67, No. 4, p. 1421-1430, 2015.
- [17] Miclos S., Popescu A., Savastru D., Baschir L., “Salinity optical sensor based on surface plasmon resonance structure with As₂S₃ waveguide”, *Macromolecular Symposia*, Volume:396, Issue:1, Special Issue: SI, Article Number 2000328, Published: APR 2021.
- [18] H. A. Macleod, *Thin-film Optical Filters*, McGraw Hill, New York, 1988
- [19] <https://refractiveindex.info/?shelf=glass&book=BK7&page=SCHOTT> (accessed on Aug. 20, 2021)
- [20] <https://refractiveindex.info/?shelf=main&book=Au&page=Johnson> (accessed on Aug. 20, 2021)
- [21] <https://refractiveindex.info/?shelf=main&book=As2Se3&page=Joseph-400nm> (accessed on Aug. 20, 2021)