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SURFACE PLASMON RESONANCE AND PHOTOINDUCED DICHROISM IN AMORPHOUS CHALCOGENIDE As_2S_3 FILMS

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Abstract. We report on experimental investigations of a plasmonic structure that contains an amorphous chalcogenide As_2S_3 thin film as waveguide. A BK7 glass prism, which has the refractive index much smaller than that of the waveguide, was used to couple the light. The reflected light may be modulated upon illumination with a polarized beam. The reflected light intensity preserves his value after stopping the illumination with in-plane polarized blue light. The reflected red light intensity can be restored with a blue beam of perpendicular polarization.

Key words: surface plasmon resonance, plasmonic waveguides, amorphous chalcogenide films, optical memory.

1. INTRODUCTION

After the discovery of surface plasmons [1–3] a lot of papers have been published in the last years concerning theoretical investigations and experimental characterizations [3–7] of the surface plasmon resonance phenomenon. Nanostructures (for instance, multilayered structures containing chalcogenide thin films) with thicknesses less than 15 nm have attracted a significant interest due to their unique chemical and physical properties and potential applications in diverse areas such as enhancement of Raman scattering, catalysis, sensing, nanofabrication for the next generation of electronic devices, photoluminescence, bio-light emission devices and solar cells. Also, another interesting application could be the development of all-optical memory using photo-induced optical transmission that occurs in films of semiconductor chalcogenide glasses after the irradiation with polarized light. Low loss planar waveguides can be realized using a multilayer structure of As_xS_{1-x} chalcogenide films with different chalcogen concentrations.

In the last years the photoinduced phenomena in chalcogenide glass thin films attracted the attention of physicists and engineers [8–12] due to possible practical applications. Photoinduced optical anisotropy [13] is the emergence of dichroism and/or birefringence in an initially optically isotropic chalcogenide film under the action of linearly polarized light. This effect is explained by the orientation of interatomic bonds or specific defects of the glass, leading to the appearance of some optical axis with a direction determined by the polarization vector of the exciting light. Amorphous chalcogenide glasses display the highest photoinduced effects among other materials. However, the effect is pretty small, on the order of 10^{-3} as compared with glass-crystal phase-changed materials like $Ge_2Sb_2Te_5$ widely used as optical memory in the mass production of CD/DVD disks. However, the phase-change phenomenon may have limited fastness because it is a thermo-optical effect.

The modulation of the light can be improved if the amorphous chalcogenide film is placed in a resonance structure. The aim of this paper is the experimental investigation of surface plasmonic resonance (SPR) light modulator, which contains an As_2S_3 amorphous film as waveguide. From reasons of practical applications, the opportunity to use prism with low refractive index such as the BK7 glass is examined, in order to achieve SPR with waveguide modes. The structure can be useful for the practical realization of optical memory photonic devices.

2. A BRIEF THEORETICAL STUDY

Multilayered structures have additional functionalities related to the confinement of the electromagnetic field. Among others, such structures provide the coupling of light into planar waveguide structures that can support both TM and TE modes. The plasmonic waveguides contain at least one metallic medium that has a complex-valued dielectric constant. As a result, the waveguide propagation constants are complex numbers. Finding the numerical solutions for the propagation constants within these structures is cumbersome; see, for example, Ref. [14], so that finding of a suitable analytical form for the characteristic equation, when is possible, appears to be a necessity.

The way is to solve the Helmholtz wave equation that results from the Maxwell's equations. Assuming the one-dimensional case, harmonic time dependence and homogeneous media, the following wave equation for TM modes may be written as [3]:

$$\frac{\partial^2 \vec{H}_y}{\partial x^2} + \left(k_0^2 \varepsilon - \beta^2\right)\vec{H}_y = 0, \quad (1)$$

where $k_o = \omega/c$ is the wave vector of the propagating wave in vacuum. The complex parameter $\beta = k_z$ is called the propagation constant of the traveling waves. The equation above is valid for each layer. The continuity conditions should be applied as a result of field continuity and the fact that the propagation constant β_x is the same in each layer. For the four-layer structure like Prism (semi-infinite)-Metal (of thickness *d*)-Dielectric waveguide (of thickness *a*)-Air (semi-infinite), the system of six equations can be solved analytically; for more details, see the paper [15].

The rather complicated expression obtained for the propagation constant is the following:

$$\left(\frac{1+\dfrac{r_1-r_4}{r_1+r_4}e^{-2k_1\cdot a}}{1+\dfrac{r_2+r_3}{r_2-r_3}e^{2k_2 d}}\right)=\left(\frac{r_1}{r_2}\right)\cdot\left(\frac{1-\dfrac{r_1-r_4}{r_1+r_4}e^{-2k_1\cdot a}}{1-\dfrac{r_2+r_3}{r_2-r_3}e^{2k_2 d}}\right). \tag{2}$$

Here $r_i = k_i/\varepsilon_i$ and k_1, k_2 are the wave vectors in dielectric waveguide film and metal, respectively.

By applying some transformations in the field of complex numbers, Eq. (2) may be brought to a simpler form:

$$d=\frac{\arctan f+\arctan g+m\cdot\pi}{\bar{k}_2}. \tag{3}$$

Thus the above *characteristic equation* for the four-layer structure has the same form as the equation obtained earlier by Marcuse [16] for the three-layer lossless waveguide structure. The difference consists of more general values for the coefficients *f* and *g*; see Ref. [15] for more details. Now, the numerical simulations for the propagation constant may be carried out. We used the same method as in paper [17] for the three-layer structure, where the gold film was considered to be thick. The structure that is considered for experimental investigations consists of a prism made of the BK7 glass, a gold film of thickness 50 nm, a thin As_2S_3 amorphous film, and air. The results for the dependence of the dielectric waveguide thickness d on the effective refractive index $N_{ef} = \beta/k_0$ are presented in Figure 1.

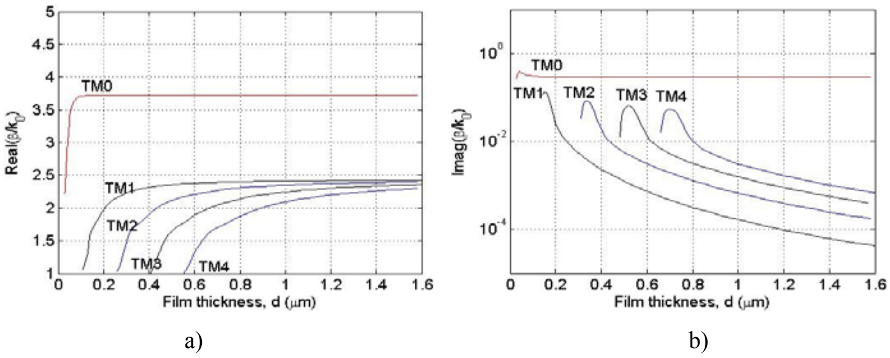

Fig. 1 – The real part (a) and imaginary part (b) of the propagation constant for the TM modes. The simulation parameters were a = 50 nm and λ = 632.8 nm.

The resonance conditions correspond to the angle θ incident on the prism base for which the condition $n_p\sin\theta = N_{eff}$ is satisfied. As our prism has the refractive index $n = 1.51$ it means that the modes for which the effective index exceeds this value cannot be excited. The following conclusions can be drawn from Fig. 1: a) the mode TM_0 can never be excited with a prism made from the BK7 glass as the effective refractive index is always higher than 1.51; b) only one mode at a time can be coupled for special selected thicknesses. For example, for a film with thickness $d = 626$ nm, only the TM_4 mode can be coupled for which the effective refractive index is about 1.3.

3. EXPERIMENTAL STUDIES

3.1. EXPERIMENTAL SETUP

An experimental setup, shown in Fig. 2, was fitted to check the validity of the model. The polarized beam from a He-Ne laser is directed to the BK7 glass coupling prism. The polarization of the laser is set in the plane of incidence so that the TM modes can be investigated.

The plasmonic structure consists of a chipset made up of a glass slide on which is deposited a thin metal film, about a 50 nm thickness gold film. The chipset is a standard one marketed by various companies for plasmonic SPR-based systems. We used a 50 nm XanTec bioanalytics [18] type AU bare gold films designed for plasmonic bio-sensor applications. The actual thickness of the gold film measured by profilometer was 46 nm. AFM microscopy analysis showed a good homogeneity of the surface of the gold film with the roughness of 2.0–2.5 nm. Over the gold film, an amorphous chalcogenide As_2S_3 film was deposited by thermal evaporation in vacuum of $6.6\cdot10^{-4}$ Pa. Bulk materials synthesis was performed under previously reported conditions [19]. As_2S_3 granular material for evaporation was placed in the tantalum resistive evaporator. The film deposition speed was 2–3 nm/s. The film thicknesses were chosen based of numerical simulations presented in Ref. [15].

The As_2S_3 film thickness measured by the profilometer varies between 610 nm to 630 nm on the 10 × 10 mm surface. This complex Au-As_2S_3 chipset is attached to the BK7 prism by using index matching oil. Cargille Labs. [20] microscope immersion oil of type A with the refractive index $n = 1.51$ was used.

The prism with the attached plasmonic structure is mounted on a rotating table, the axis of which is perpendicular to the plane of the figure. Thorlabs NR360S continuous rotation stage [21] with stepper motor actuator and 1 arcsec resolution was used in order to ensure the measurements of the peak shapes with high accuracy. The radiation reflected by the plasmonic structure is measured by a digital powermeter model Gentec Solo PE. The powermeter is mounted on another table, co-axial to the first one, which provides a rotational angular velocity twice the rotation angular speed of the prism. Such setup permitted to maintain fixed position of the reflected spot on the powermeter head.

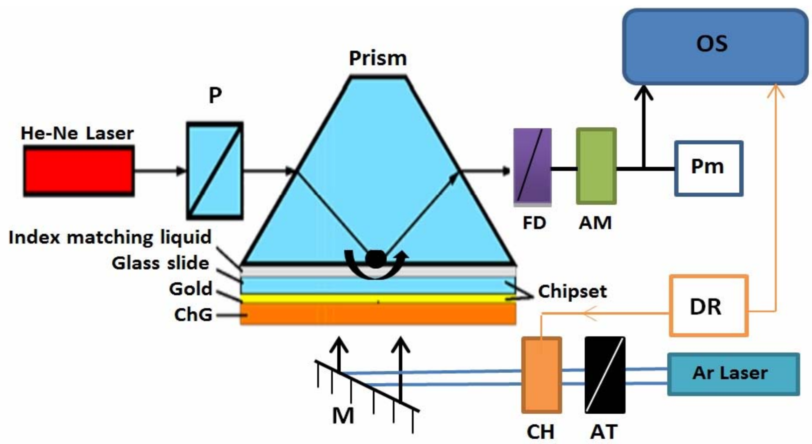

Fig. 2 – Experimental setup for the realization of SPR with As_2S_3 waveguide modes. The chipset structure for SPR contains chalcogenide and gold films deposited onto oxide glass slide. Legend for abbreviations: P – polarizer; FD – photodiode; AM – electronic amplifier; Pm – power meter; OS – oscilloscope; DR – the driver for light shutter CH; AT – polarizer-attenuator; M – mirror.

3.2. SPR RESONANCE WITH As_2S_3 WAVEGUIDE STRUCTURE

The experimental plot representing the dependence of the reflected light intensity *versus* the incidence angle is shown in Fig. 3 (the blue curve). The angle on the graph represents the incidence angle Θ to the normal of the prism base. This one is calculated from the angle between the laser beam and the normal on the incident plane. Zero angle value corresponds to normal incidence of the laser beam. It was measured with accuracy better than 0.1 degree.

The proposed configuration has two advantages: a) it is not necessary to perform the film deposition directly on the prism base, as is more expensive as the use of slide samples and b) the proposed configuration allowed the use of high quality commercial gold film deposited on planar substrates. In the same vein, one and the same prism was used for multiple experiments with different film thicknesses. The provided simulations indicated that, for certain chalcogenide film thicknesses, some plasmonic waveguide modes can be excited using a BK7 glass prism that has the refractive index (n = 1.51) much lower than the refractive index of the chalcogenide amorphous film (n = 2.45). The optical field cannot be coupled into the TM_0 mode since the effective refractive index (β/k_0) of this mode exceeds the refractive index of the prism.

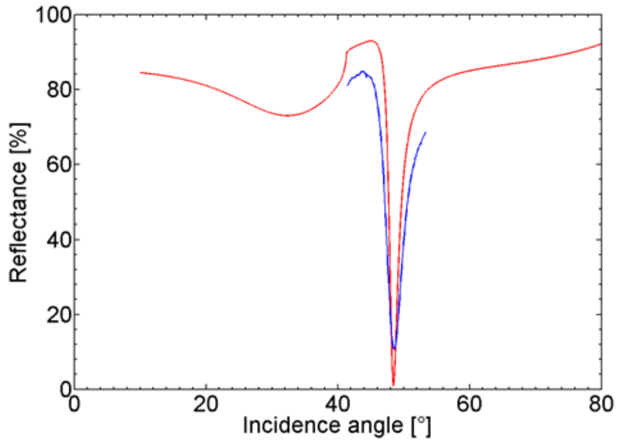

Fig. 3 – The experimental resonance curves for amorphous As_3S_3 dielectric waveguides (blue) and the calculated reflectance (red) as function of the incidence angle.

The minimum reflectance was obtained for the angle of 48.2 degree when a film with thickness of 626 nm was used.

3.3. LIGHT MODULATION IN SPR STRUCTURES WITH AMORPHOUS As_2S_3 FILMS

Amorphous chalcogenides are known as materials that support modification of the optical constants during or in the outcome of the illumination with light. It can be expected that low changes of the refractive index of amorphous film may conduct to high changes of the reflected light due to a sharp peak of SPR. Similar effects occur in the case of SPR based chemical sensors, when the considered feature was the refractive index of the environment.

To provide experimental investigations the setup shown in Fig. 2 was completed with external illumination module containing light source, polarizer-attenuator, shutter, and mirror. The lighting was done with a 30 mW multiline CW argon laser, the main power of which was contained in the lines with wavelength 488 nm and 514 nm. The light reflected from the plasmonic structure was registered by a silicon photodiode connected to a two-channel digital oscilloscope. The electronic driver runs the shutter and gives the synchronization signals for oscilloscope. The plasmonic chipset characteristics were as in the previous section.

By rotating the table with the designed structure it was obtained the SPR reflection of red light close to minimum. The laser beam is linearly polarized and the polarization was changed from the in-plane incidence to the perpendicular incidence by using a half-wavelength plate. The change of blue light polarization leads to the intensity changes of the red laser beam. The signal on the oscilloscope has the shape presented in Fig. 4.

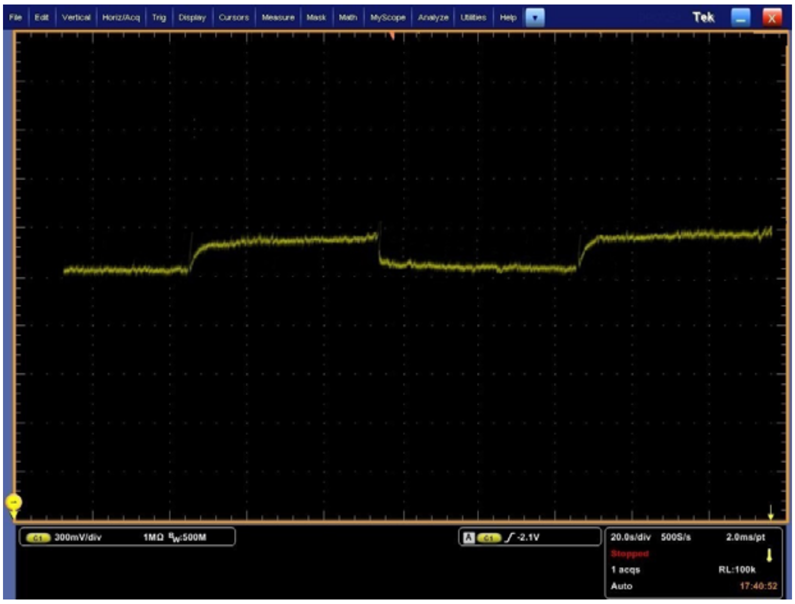

Fig. 4 – Change of the reflected light due to illumination with the blue polarized light.

We were able to get the signal changes up to 10%. The commutation time from one value to another one was fractions of seconds and depended on the intensity of the blue laser. The intensity of the reflected signal keeps the value even after the irradiation has stopped. We experimentally demonstrated a proof of concept optical memory device.

4. DISCUSSION OF THE RESULTS

The interpretations of the experimental results were made in two steps. In the first step, the structure used for numerical calculations as well as for experiments was a three layer BK7 (prism)-Au (46 nm film)-Air configuration, *i.e.* without the chalcogenide film. The aim was to determine the actual value of gold optical constant we have used. The minimum reflectance that corresponds to the plasmon-polariton resonance was 48.2°. The wave was confined to the air-Au film boundary. The BK7 glass is a well-standardized material with the refractive index $n = 1.5151$. The gold optical constants (n, k) were found by different authors and are presented in Table 1.

Using these data, different values for the resonance angles were calculated and are shown in Table 1. The experimental value for the plasmonic resonance angle of 44.2° was determined for the wavelength 632.8 nm. This value best fits with the data of Rakic *et al.* [22], which give the calculated angle value of 44.17°. Rakic *et al.* [22] have developed a phenomenological model to determine the optical constants for many metals. For gold they used the experimental data of Theye [23].

Table 1

The calculated SPR angles for different optical constants of gold

Nr.	Refractive index, n	Extinction coefficient, k	Resonance angle, θ [°]	Reference
1	0.184	3.431	43.835	Johnson [24]
2	0.196	3.256	44.170	Rakic *et al*. [22]
3	0.707	3.322	44.405	Gao *et al*. [25]

In the second step, the determined values of the gold optical constants ($n = 0.196$ and $k = 3.256$), were used to investigate numerically the four layer plasmonic resonance structure. The best matched curve presented in Fig. 3 (red), was obtained by using the following parameters for the chalcogenide film: the thickness 600 nm (the profilometer data indicated 626 nm ± 2%) and the refractive index of 2.43. This value of the refractive index complies with the value of 2.41 measured by waveguide m-line spectroscopy [26].

According to the simulations, the measured resonance angle for the thickness of 600 nm corresponds to the TM_4 waveguide mode. As is shown in Fig. 5, at the external boundary of plasmonic structure, the higher waveguide modes have also the higher field values. That means that a higher sensitivity to the refractive index changes is possible.

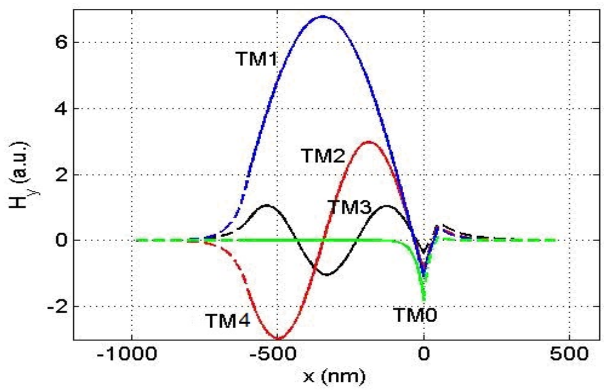

Fig. 5 – Magnetic field distribution of the TM_0-TM_4 modes for the plasmonic structure with As_2S_3 amorphous chalcogenide waveguide with the thickness of 600 nm. The dielectric-metal interface corresponds to $x = 0$.

The SPR used for light modulation is based on photoinduced change of the optical constants in amorphous materials, a phenomenon that depends on the exposition doze, *i.e.* on the power-time multiplication. By using kW short-pulse lasers significant reduction of the commutation time can be obtained. The reset time can be also shortened in a forced mode by irradiation with intense light that is polarized in perpendicular direction. This fact differs from the situation used in CD/DVD disks, where the reset time is a free parameter that depends only on the thermal conductivity of the corresponding material.

5. CONCLUSIONS

The SPR structure supports several waveguide modes for finite thicknesses of the metal film and finite thicknesses of amorphous chalcogenide material even if the prism refractive index is much lower then the waveguide refractive index. The prism made by the BK7 glass (with $n = 1.51$) can be used for coupling the light into chalcogenide As_2S_3 amorphous film waveguide (with $n = 2.45$). For some well-defined thicknesses, the light can be coupled into plasmonic waveguide modes. The attractiveness of using amorphous chalcogenide films is that they can be used as light sensitive optical materials due to photoinduced changes of the refractive index. The experiment demonstrated the high sensitivity to the polarized light illumination of the chalcogenide films in the SPR configuration. The structure presents much interest for the development of optical switches, two-dimensional memories, and plasmonic sensing elements.

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