JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 13, No. 4, April 2011, p. 412 - 415

Enhancement of photo induced changes due to plasmon field in amorphous chalcogenide thin film structure

STEPAN CHARNOVYCH
Department of Experimental Physics, University of Debrecen, Bem sq. 18/a,4026, Debrecen, Hungary

Interaction of non-destructive laser light with amorphous chalcogenide semiconductor films results specific structural changes and related effects of optical recording and memory, which in general originate from electron-hole excitations, defect creation or modification and subsequent atomic motions. As far electron processes are sensitive to the electric fields, the light stimulated changes can be influenced by plasmon fields. We have investigated the effect of the plasmon field on the photo-darkening or bleaching and also on induced thickness changes in thin chalcogenide films, specifically in As_2S_3 and As_2Se_3 compositions, which are the most known and frequently used for investigations of photoinduced effects. Thin film structures built of gold nanoparticles (GNP) deposited on the silica glass substrate and covered by an amorphous film were used for investigations. Correlation was observed between the surface plasmon resonance in the selected spectral region of illumination of investigated samples and the characteristics of photo-darkening and bleaching, thickness change, which show on the possibility to increase the efficiency of optical recording in chalcogenide films.

(Received October 13, 2010; accepted April 11, 2011)

Keywords: Thin amorphous chalcogenide films, Photo-induced effects, Gold nanoparticle, Plasmon enhancement.

1. Introduction

Thin films of amorphous chalcogenide glasses are well known as materials where different photo-induced effects like photo-darkening and bleaching, local expansion or contraction, changes of the reflectivity and of the refraction index take place [1-4]. They are important for the development of materials for optical recording and memory devices. A lot of investigations of the photo-induced changes in amorphous chalcogenides are known, some models are developed but the real mechanism of light-induced processes and structural transformations are still not completely clear. That is why for getting more facts about these processes the research and development of new compositions and structures is still going on. One important task is the sensitivity of optical recording in the materials like As_2Se_3 for red laser and As_2S_3 for green laser illumination: sensitivity is rather low due to the absence of internal amplification [1-7] and should be improved.

Some metals are widely used for exciting surface plasmon resonance (SPR) on their surface and enhancement of electron processes in the surrounding media. Gold is one of the most popular and important because of the manifestation of optical resonance in the visible spectral range [8]. The SPR appears due to the excitation of surface plasmons by light for planar metal surfaces at special matching conditions, while the localized surface plasmon resonance (LSPR) is rather easily observed in nanometer-sized metallic structures [9]. The last are widely used for the development of ultrahigh-sensitive fluorescence measurements, sensing, semiconductor devices [10-12] and even for optical data storage [13].

Because of the localized electromagnetic field amplification near the nanoparticle the enhanced interaction of the exciting light with surrounding media occurs and electron-hole processes in it as well as the interatomic bonds and the structure in the whole can be more easily altered. We used this effect for the enhancement of photoinduced transformations and so of the amplitude-phase optical recording based on the amorphous chalcogenide films made of the most widely investigated As_2Se_3 and As_sS_3 glasses.

2. Experimental

We started our experiments with fabrication of appropriate plasmonic element, suitable for optical measurements of photo-induced effects in a given chalcogenide layer. Gold nanoparticles (GNP) on a silica glass substrate satisfy the conditions for SPR in a green-red spectral range, where the selenide and sulphide glasses are most sensitive [1,2]. It is known [10-12] that the increase of the size or shape variations of the metallic nanoparticles lead to the red shifts of the SPR and we used it in our experiments. As far as the shape of the GNP deviates from the sphere the deviations (size, shape) could influence the SPR peak, as it was measured in our case. First, 30 nm thick Au layers were deposited on glass substrates. The obtained samples were annealed at different temperatures (400-600 ^{0}C) and for different times. In the result we got samples with non-spherical GNP with size distribution in a comparatively narrow range. The average size of the GNP was established with LabView 7 using pictures made in SEM (Hitachi S-4300). The optical transmission spectra of the prepared samples were measured with Shimadzu UV-3600 spectrophotometer. It was shown that the SPR peak depends on the average size of the Au particles produced on the silica glass substrates (Fig.1).

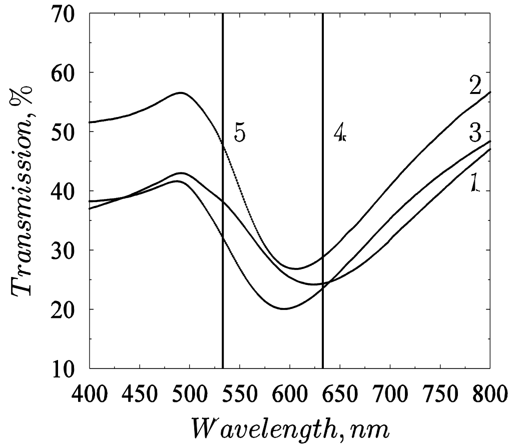
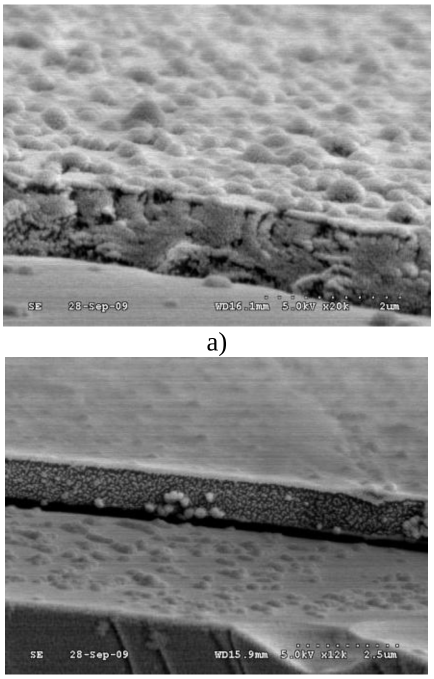


Fig. 1 Optical transmission spectra of the GNP with different average diameter of the particles (1 – 60 nm, 2 – 75 nm, 3- 90 nm) and the emission line of the recording lasers (4- red, 5-green).

The prepared samples with Au nanoparticles were covered by a 700 nm thick thermally evaporated chalcogenide layer (As_2Se_3 or As_2S_3).These layers are sensitive in the red and green spectral range respectively, therefore the investigated samples were irradiated with red (λ=633 nm, output power P=7mW) or green (λ=533 nm, output power P=17mW) laser beam through a 1,2 mm hole in a mask. At our experimental conditions the maximum light intensity at the surface was near 150 mW/cm^2 for the red laser irradiation and 350 mW/cm^2 for the green one. The change of transmission versus irradiation time was detected with power meter setup (ThorLabs PM100). The thickness of the layer as well as its changes were measured by Ambios XP-1 profile meter and checked by Veeco AFM. Optical transmission spectra were used for calculations of the refractive index by Swanepoel method [14] which was supplemented with data on thickness change under illumination.

3. Results and discussion

Localised surface plasmons (LSP) are collective electron charge oscillations in metallic nanoparticles when excited by light. They are associated with enhanced near field at resonance and such a field is localized at the nanoparticle and decay away from the nanoparticle/dieletric interface into the dielectric background. Light intensity enhancement is a very important aspect of LSP resonance and the localization means LSP has very high spatial resolution (subwavelength) limited only by the size of nanoparticles. The distribution and surface density (surface coverage) of nanoparticles on a substratum should influence the integral effect i.e. the volume where enhanced electron-hole processes and changes take place. So we created LSP by illumination of the nanoparticles in a complex samples (Fig. 2, a and b) and observed the effect of LSP on the photo-induced changes in the system.



a)

b)

Fig. 2 a) and b) SEM pictures of the As_2S_3 - GNP system before and after irradiation. Broken edge of the layer on silica glass substratum with GNP is visible as well as thin carbon layer used for surface discharging.

Optical darkening and changes of the reflective indexes and of the coefficient of absorption, as well as the red shift of the fundamental absorption edge were observed at the initial stage of illumination in both types of samples prepared as pure films or structures with GNP. The change of the transmitted intensity I relative to the initial I_0 for a given sample with time t during illumination $\gamma=\Delta(I/I_0)/\Delta t$ was taken as a rate of the photo-induced change. It was established that the rates of the changes were different: γ was larger in the case of As_2Se_3 (16,5*10^{-3} s^{-1}) than in the case of As_2S_3 γ=4,2*10^{-3} s^{-1}. It was true for Au-containing structures too, where the process rate in both cases was faster as in the single layers, and depends additionally on the size of the nanoparticles (see Fig 3).

An unusual effect of photo-induced bleaching appeared in GNP-chalcogenide structures: effect was different from the simple darkening with saturation in a single chalcogenide layer. In the sample that contains GNP after initial process of darkening the transmission started to increase. It was established that the rate of decreasing and increasing of transmission depended on the size of the nanoparticles, so on the plasmon wavelength in the given structure. In the case of the samples that contain GNP with average diameter 90 nm and with plasmon peak wavelength closest to the wavelength of the laser light wavelength we observed the fastest and the most significant changes (thickness, refractive index, coefficient of absorption). We calculated γ in As_2Se_3 – GNP system for different particle sizes and they were the following: 1 – 2,6 *10^{-2} s^{-1}, 2 – 2,2 * 10^{-2} s^{-1}, 3 – 1,8 * 10^{-2} s^{-1}, 4 – 17,3*10^{-2} 1/s (see Fig. 3). The same was observed and calculated for the As_2S_3 – GNP system:1 – 5,9 * 10^{-3} s^{-1}, 2 – 7,3 * 10^{-3} 1/s, 3 – 11,3 * 10^{-3} 1/s, 4 – 4,2 * 10^{-3} 1/s (see Fig. 3. too).

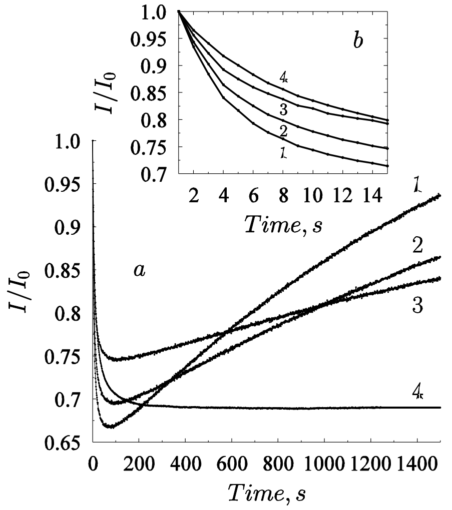


Fig. 3 a) Time dependences of the optical transmission on the irradiation time in a single As_2Se_3 layer(4) and structures with GNP (sizes 60 (1), 75 (2) and 90 nm (3)). b) the same at the initial stage of irradiation.

As we see from the obtained data in the samples that consists of GNP with plasmon absorption peak nearer to the wavelength of the illumination the changes are more efficient as in the system with GNP where the plasmon peak is more shifted from the illumination wavelength. Also we established that the plasmon absorption peak had a red shift with increasing size and it is closer to the red wavelength of illumination that is why we observed more efficient changes in the As_2Se_3 - GNP system.

In the system with GNP after the initial decrease of the optical transmission under the continuous illumination it started to increase and the bleaching rates were GNP-size dependent in a similar way as in the case of initial darkening i.e. the faster was the increase for the sample that possessed the faster darkening rate. It was interesting also to measure the possible thickness change of the layer under illumination, since the local expansion-contraction effects are complementary with other photo-induced processes in chalcogenides, although the relations are not completely clear yet [15]. The results are presented in the Table 1 and Table 2.

Table 1. The deviations, Δ (+ increase, - decrease) as well as the changes in % of the refractive index n, layer thickness d and absorption coefficient α measured in as-deposited and illuminated single As_2Se_3 layer and in the same material with GNP at the stage of saturation of changes.

	As_2Se_3		As_2Se_3+GNP	
	Δ	%	Δ	%
n	0	0	+0,01	0,39
d, nm	-23	3,3	-60	8,2
α, cm^{-1}*10^4	+0,02	2,02	+0,03	1,51

Table 2. The deviations, Δ (+ increase, - decrease) as well as the changes in % of the refractive index n, layer thickness d and absorption coefficient α measured in as-deposited and illuminated single As_2S_3 layer and in the same material with GNP at the stage of saturation of changes.

	As_2S_3		As_2S_3 +GNP	
	Δ	%	Δ	%
n	0	0	+0,01	0,42
d, nm	-20	2,86	-50	6,85
α, cm^{-1}*10^4	+0,04	2,8	+0,03	1,23

It should be noted here, according to our previous experiments, that the local volume increase in illuminated spots above the commonly known ≈1% occurs at low, $I \approx$ 10 mW/cm^2 intensities, which is different for different compositions. The increase of the illumination intensity leads to the decrease of expansion and even hole formation, i.e. local contraction. One possible explanation of this effect was proposed in [16], which also relates to the efficiency of local charge carrier generation and transport. If so, the presence of plasmon field should act like the increase of the excitation intensity, and the contraction should appear at lower illumination intensities in comparison with pure chalcogenide films without GNP. The optical bleaching of the samples that include GNP can be explained with the change of *exp(α·d)* in the exponential dependence of transmission because the decrease of the thickness was more significant for this system as for pure chalcogenide layer where it appears only in As_2S_3 layer at the given illumination intensities or at much higher intensities as presented in the above mentioned experiments for selenide. That is why we observed a decrease of the thickness (for As_2S_3) and increase of it (for As_2Se_3) in the samples without GNP. Contrary, in the systems that include GNP we observed decrease of the thickness in all our experimental conditions. The rate of the changes depends on the size of the GNP and in this way on the plasmon frequency. As in the case of changes of the transmission the scale of the thickness changes was the most significant for the system that includes the biggest average size GNP and so the excitation wavelength was closer to the resonance.

Explanation of the enhancement effects relates to the initial stage of the photo-induced effects in chalcogenide glasses, which consists of generation of electron-hole pairs, creation or modification of defects like dangling bonds or changed coordination of chalcogen [17,18] as well as to the existence of localised electric field of plasmons. The last should enhance the above mentioned electron processes, influencing the rate and the final value of the structural changes up to the small shifts of atoms (first stage of volume expansion) or further diffusion and mass transport at the presence of additional driving forces (the gradients of excitation intensity, polarization of the light beam).

To support the above mentioned experimental results and assumptions about the role of surface plasmons in the photo-induced processes in chalcogenide glasses, we have analysed the conditions of plasmon generation and its influence in the given system of GNP in a glass matrix. The simplest way to approach the problem is to treat each material as a homogeneous continuum, described by a frequency-dependent relative permittivity between the external medium and the surface. This quantity, hereafter referred to as the materials' "dielectric constant," is complex-valued. In order for the terms which describe the electronic surface plasmons to exist, the real part of the dielectric constant of the metal must be negative and its magnitude must be greater than that of the dielectric. To analyze the effect of the LSPR on the photoinduced changes in chalcogenide system we need to look after the necessary conditions of the surface plasmon resonance. They are the following [9]:

1. Dielectric constant of the surrounding medium has to be positive.

2. Real part of the dielectric constant of the GNP has to be negative.

The first condition is realized, because the dielectric constant ε of the surrounding medium, in our case the chalcogenide layers, equals to 8 for As_2S_3, and to 10 for As_2Se_3 [19]. But we have no data about the real part of the dielectric constant of the GNP. Let’s calculate for the largest grain size GNP system, where the average diameter of the GNP was 90 nm. For calculations of the dielectric constant of the GNP we used Mie-theory, because for sizes greater than a few tens of nanometer the quasi-statistic approximation is no longer valid and the interaction of an electromagnetic wave with a nanoparticle must explicitly take into account the spatial variations of the field over the size of the object. According to this theory we can calculate the dielectric constant of the gold nanoparticles using certain equations [20-22]. In our case the real part of the dielectric constant is -0.35, the imaginary part is 0.13. So the second condition is also valid in our systems and theoretically the localized surface plasmons were generated in them. These allow us to estimate the penetration depth of the plasmon field [23]. For the As_2Se_3 the penetration depth is 926 nm and for As_2S_3 it is 751 nm. It means that our films were sufficiently influenced by plasmon fields.

4. Summary

Based on the general model of successive interconnected processes which occur in amorphous chalcogenide semiconductor under illumination and influence photo darkening, photo-induced volume change we have established the essential influence of surface plasmons on these effects in a complex samples, which consists of the discontinuous layer of gold nanoparticles covered by the appropriate chalcogenide layer. The investigated effect of enhanced structural transformations can be used for direct recording of holographic gratings, waveguides and other elements of integrated optics, made of chalcogenide glasses.

Acknowledgements

This work was supported by TAMOP 4.2.1.B/09-1/KONV-2010-0007. Author would like to thank to Cs. Cserháti for making SEM pictures and S. Kokenyesi for fruitful discussions.

References

[1] K. Shimakawa, A. Kolobov, S. R. Elliott, Adv. Phys. **44**, 475 (1995).
[2] V. M. Lyubin, in: A. Kartuzhansky, Ed. Khimia (Eds.), Nonsilver Photographic Processes, 1984 (in Russian).
[3] Mihai A. Popescu, Non-Crystalline chalcogenides,(Kluver Academic Publisher, Durdrecht, 2000).
[4] Y. Sakaguchi and K. Tamura, J Mater Sci: Mater Electron **18**, 459 (2007).
[5] M. Chomát, D. Ležal, I. Gregora and I. Srb, J. Non-Cryst. Solids **20,** 427 (1976).
[6] Mario Bertolotti, Francesco Michelotti, Valentin Chumash, Pavel Cherbari, Mihai Popescu, Sorin Zamfira**,** J. Non-Cryst. Solids **192& 193**, 657 (1995).
[7] Sati, Dinesh C. Kumar, R. Mehra, R. M. Jain, H. Ganjoo, Ashtosh, J. App. Phys. **109**, 123105 (2009).
[8] Richard B M Schasfoort and Anna J Tudos, Handbook of Surface Plasmon Resonance, (RSC publishing, Cambridge, 1998).
[9] Hutter E, Fendler J. Adv. Mater. **16.** 1865 (2004).
[10] Susie Eustis and Mostafa. A. El-Sayed Chemical Society Reviews, **35** , 209 (2006).
[11] T. A. El-Brolossy, T. Abdallah, M. B. Mohamed, S.Abdallah, K.Easawi, S.Negm, H.Talaat, Eur. Phys. J. Special Topics **153**, 361 (2008).
[12] Amanda J. Haes, Richard P. Van Duyne, Analytical and Bioanalytical Chemistry, **379**, 920(2004).
[13] Ovshinsky, S. R., Strand. D., Tsu, D., U. S. Patent no. 7292521, (2006).
[14] W. Swanepoel, J. Phys. E: Sci. Instrum. **16,** 1224 (1983).
[15] M. L. Trunov, P. Lytvyn, V. Takats, I. Charnovych, S. Kokenyesi, J. Optoelectron Adv. Mater. **11**, 1959 (2009).
[16] Yu. Kaganovskij, D. L. Beke, S. Kokenyesi, Appl. Phys. Lett. **97**, (2010) 061906
[17] J. Hegedus , K. Kohary, S. Kugler, J. Non-Cryst. Solids, **352**, 1587 (2006)
[18] J. Hegedüs, K. Kohary, D. G. Pettifor, K. Shimakawa, S. Kugler, Phys. Rev. Lett. **95** 206803 (2005).
[19] Mihai. A. Popescu, Aide-memoire: chalcogenides and general tables for material scientist, INOE, Bucharest, 2005
[20] T. Mortier, Ph.D. Thesis, College van Dekanen, University of Twente, The Netherlands, 1992.
[21] S. Link, M. A. El-Sayed. J. Phys. Chem. B, **103,** 4212 (1999),
[22] U. Kreibig, C. V. Fragstein. Z. Phys. **224**, 307 (1969).
[23] T. Neal, K. Okamoto, A. Sxherer, Optics Express, **13**, 5522 (2005).

---

[*] Corresponding author: csari86@gmail.com