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Plasmon assisted photoinduced surface changes in amorphous chalcogenide layer

S. Charnovych [a,*], I.A. Szabó [b], A.L. Tóth [c], J. Volk [c], M.L. Trunov [d], S. Kökényesi [a]

[a] Department of Experimental Physics, University of Debrecen, Bem sq. 18/a, 4026, Debrecen, Hungary
[b] Department of Solid State Physics, University of Debrecen, Bem sq. 18/b,4026, Debrecen, Hungary
[c] Research Institute for Technical Physics and Materials Science, Budapest, Hungary
[d] Uzhgorod National University, Uzhgorod, Ukraine

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ABSTRACT

The influence of the localized surface plasmon fields on the light stimulated transformations in amorphous chalcogenide films was investigated. It was established that both in the gold nanoparticle array-chalcogenide film and in the gold film with nanohole array-chalcogenide film composites the plasmon fields, induced during the laser illumination of the structures, increase the efficiency of structural transformations, the related photodarkening or bleaching, as well as of the volume change, surface deformations. The results, obtained for structures with $As_{20}Se_{80}$ amorphous layer, can be applied for other selected chalcogenide layers and fabrication of locally driven information recording media.

1. Introduction

Amorphous chalcogenide semiconductor layers exhibit well known photo-induced structural changes under the influence of photons with energy close to the band gap (E_g) energy [1–3]. Photo-induced expansion, surface deformation and lateral mass transport were detected by investigation of periodic surface relief formation in $As_{1-x}Se_x$ layers via in situ atomic-force microscope measurement [4]. It was shown [5] that holographic recording of surface relief in $As_{20}Se_{80}$ glasses has at least two components: a fast, but with a rather small change of the thickness, which can be related to stimulated volume expansion as observed by Tanaka [6] in As_2S_3 and a slower but a giant one associated with light induced lateral mass transport [7,8]. It was shown that the mass transport in amorphous chalcogenides due to the polarized illumination is controlled by anisotropic volume diffusion [9,10].

Stimulated darkening or expansion and mass transport also appear when chalcogenide layer is irradiated by e-beam and build in electric fields are created [11,12]. Consequently the electric field should influence the generation of electron-hole pairs, creation of defect states, mass transport and so the plasmon field of the metallic nanostructures also can be involved to the recording processes.

Surface plasmons can be excited on the metallic surface by light at special matching conditions [13]. Localized surface plasmon resonance (LSPR) can be excited more easily in nanosized metallic nanoparticles [14] or even nanohole arrays in metallic layers [15]. Gold and silver are widely used for surface plasmon resonance (SPR) measurement, because the resonant conditions (absorption maximum in a visible spectral range) are easily achieved and the technology of nanoparticles is well developed. Gold nanoparticles (GNP) on a silica glass substrate and nanohole arrays in a gold layer (GNH) with dimensions in the 5–100 nm range satisfy the conditions for SPR in green–red spectral region, where As–S(Se) glasses are the most sensitive to the illumination. It was shown previously that the plasmon resonance wavelength of the nanostructures can be controlled by changing the sizes of the nanostructures [16–18]. The electric field of an incoming p-polarized (vector **E** perpendicular to the interface) light can induce certain distribution of the surface charge density of the particle. There is a net electric field around the excited nanoparticle that is composed by superposition of an external applied field (electromagnetic wave) and the induced field of the particle. This net electric field can influence the photo-induced changes in chalcogenides as it was shown previously [19].

The aim of this work was further investigation of the effect of LSPR on photoinduced changes in $As_{20}Se_{80}$ + gold nanostructured system. For this investigation GNP and GNH were produced to create localized surface plasmons. The effect of these nanostructures on the transmission changes in chalcogenide layers due to the laser irradiation, as well as on the volume (roughness) change has been investigated.

2. Experimental

Experiments on photo-induced changes have been done on composite structures, which contained appropriate plasmonic element and a chalcogenide layer. Results were compared with data on a single chalcogenide layer. At the first step plasmonic elements – GNP or GNH – were created. Since the $As_{20}Se_{80}$ is highly sensitive just to the

* Corresponding author.
E-mail address: csari86@gmail.com (S. Charnovych).

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action of red laser light the plasmon resonance wavelength of these elements was adjusted to the red spectral region.

For creation of gold nanoparticles, first a 25 nm thick gold layer was deposited in vacuum on the silica glass substrate due to the Ostwald ripening. This sample was annealed for 4 h at 550 °C and GNP were created. The obtained samples of GNP were investigated by Scanning Electron Microscope (SEM) (Hitachi S-4300). The average size of the GNP was calculated from the SEM pictures (see. Fig. 1c) by a special program setup and it was about 120 nm. The plasmon resonance wavelength of these structures was near 630 nm.

The nanoholes in the gold layer of the same thickness, deposited on the similar glass substrate, were prepared by e-beam lithography method (see Fig. 1d). The diameter of the holes was about 200 nm because it had been shown previously [18] that nanoholes with a size of about 200 nm in gold layer have plasmon resonance close to 630 nm.

A 600 nm thick $As_{20}Se_{80}$ layer was thermally evaporated in vacuum on the above mentioned gold nanostructures. The schematic diagram of the sample structure with GNP and GNH and chalcogenide layer is presented on Fig. 1a and b. The sizes of the GNH rectangles were rather small (see Fig. 1b) to perform direct optical measurements in a GNH-chalcogenide structure. So here mostly the surface changes were investigated. The investigated structures were irradiated by red laser beam ($\lambda = 633$ nm, output power $P = 7$ mW) through a diaphragm with 1.2 mm diameter. The maximum light intensity at the surface was 600 mW/cm^2. The optical transmission spectra of the samples have been measured with Shimadzu UV-3600 spectrophotometer. The change of the transmission on the irradiation time has been detected with power meter setup (Thorlabs PM100). The layer thickness and its changes have been measured by Ambios XP-1 profile meter. Optical transmission spectra have been used for calculation of the refractive index, absorption coefficient, and absorption edge change using Swanepoel method [20]. Surface relief gratings were recorded on the samples by two coherent p-polarized laser beams with equal intensity.

The experimental set-up for transmission measurements by coherent laser beam was modified for in situ measurements of surface roughness change in atomic force microscope (AFM) (Veeco-diCaliber). Both the ChG/GNP and ChG/GNH samples were irradiated from the bottom side, while the scanning of the surface was done on the top of the samples. The samples were irradiated with the same setup as before but with lower intensity (3 mW). The process was done through a spot, whose diameter was 0.5 mm, so the laser intensity on the surface of the sample was 40 mW/cm^2. Each scan takes few minutes so the time

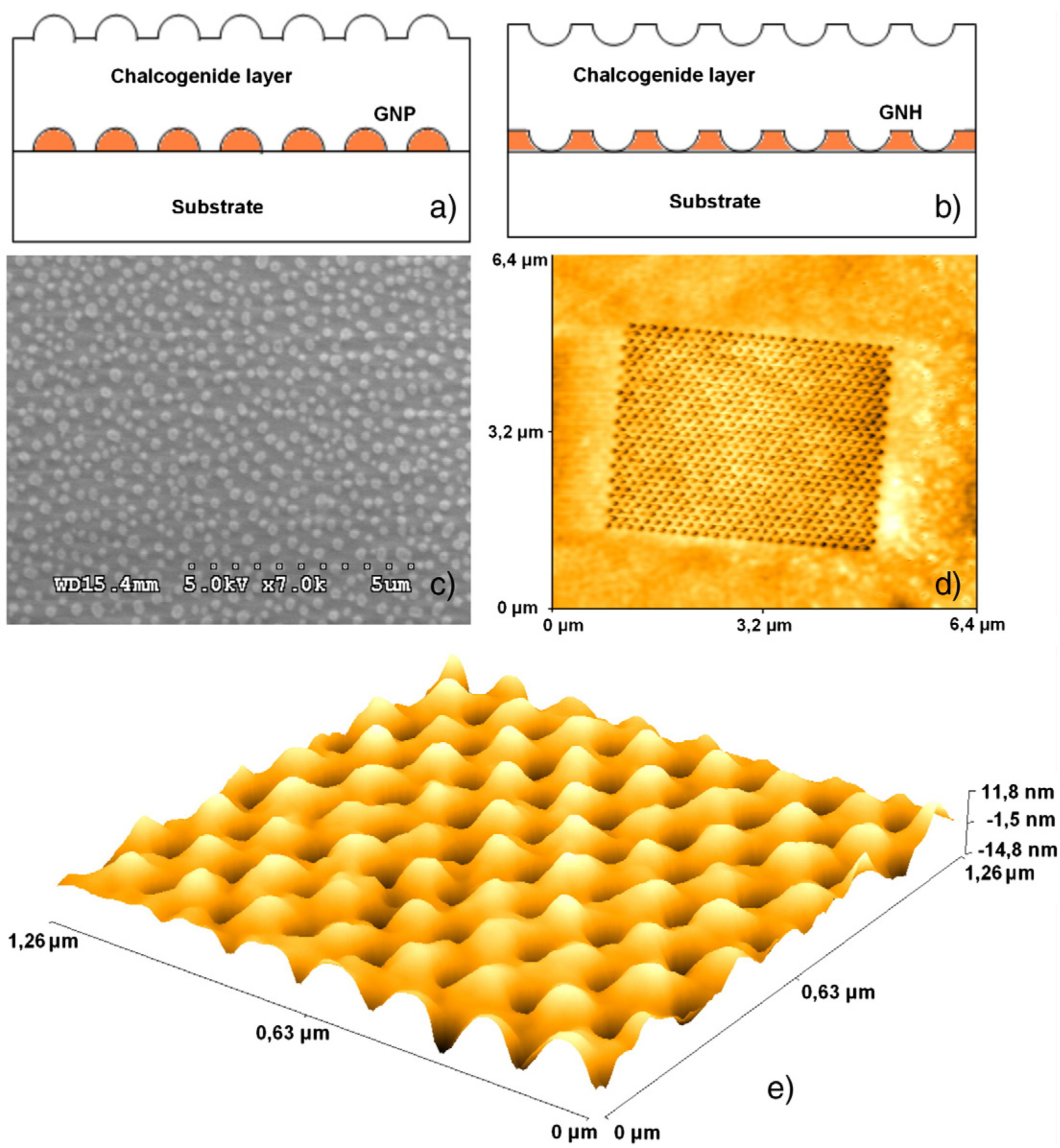

Fig. 1. a) and b) Schematic diagram of the sample structure with GNP and GNH and chalcogenide layer. c) SEM image of the created GNP structures. d) and e) 2D and 3D AFM images of the created GNH structures.