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Enhancement of laser recording in gold/amorphous chalcogenide and gold/acrylate nanocomposite layers

J. Burunkova [a], I. Csarnovics [b], I. Denisyuk [a], L. Daróczi [b], S. Kökényesi [b]

[a] ITMO University, St. Petersburg, Russia
[b] University of Debrecen, Debrecen, Hungary

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ABSTRACT

Two types of amorphous materials with the same functional purpose – direct optical recording of optical amplitude–phase surface reliefs – were investigated with the aim to establish the influence of incorporated gold nanoparticles on the recording efficiency. It was shown that the laser recording of optical reliefs on the basis of photo-polymerization of the selected acrylates or on the basis of structural polymerization–destruction like processes in chalcogenides with photo-plastic effects can be enhanced in the presence of Au nanoparticles (AuNPs). The lateral mass-transport processes at the molecular and nanoparticle levels are initiated by the non-uniformly, periodically distributed recording optical fields and increase the resulting surface reliefs in these materials, which can be used as microstructured optical elements, holographic gratings.

1. Introduction

Usually the composites unite useful properties of components to create more sophisticated materials. The novel trends in materials science favor nanocomposites which can differ from those properties of analogous composites with larger particles. This trend offers new opportunities for the creation of materials with exceeding performance for a wide range of applications including optics and holography and information technologies. Particular distributions of the nanoparticles within the polymer matrix under the light treatment is a basis for efficient holographic recording [1,2]; nanolayered composite chalcogenide films exhibit enhanced light stimulated interdiffusion and optical relief recording [3].

Gold is one of the most preferred metals which is used in glass and in polymer nanocomposites due to its exceptional stability, possible influence on the charge generation, polymerization processes and because of its plasmon resonance effects, which are easily generated and observed in 500–800 nm spectral range in dependence of the size and shape of the nanoparticles. The change of the color and the transparency due to the incorporation of different nanoparticles can be of interest in combination with other properties which favorably improve the characteristics of polymer materials, such as optical absorption or modification of refractive indices and mechanical properties under the light irradiation. The plasmon fields can influence the electron–hole processes and charge carrier generation–recombination in semiconductor chalcogenide glasses, affecting at the same time photo-structural transformations, so called photo-plasticity in these materials [4]. The problems of compatibility of AuNPs with a given matrix, the aggregation effects in monomers and glasses, and the change of spatial distributions appear frequently and stimulate intensive investigations of different fabrication as well as processing methods, first of all optical ones.

There have been several methods used for the synthesis of polymer nanocomposites that can be classified under two major categories: as physical and chemical methods. Physical methods imply direct introduction of gold nanoparticles to the matrix, for example by intercalation, whereas chemical methods are in-situ processes of creating gold nanoparticles in the matrix. For example, gold–poly(methyl methacrylate) nanocomposites were prepared by irradiating spin-coated films containing the polymer and the gold precursor dissolved in acetone [5]. The reduction of gold ions results in the formation of Au that nucleates and grows within the polymer film. It was shown that gold nanoparticles (AuNPs) with different shapes can be formed this way. Such a chemical rout can be also applied for Au–silica glass nanocomposites, but is not used for chalcogenide glasses. In our work we used direct physical routs to introduce preformed gold nanoparticles with known dimensions and plasmon resonance characteristics to the chalcogenide glass or acrylates and have investigated the influence of these nanoparticles on the characteristics of laser processing and optical relief recording in nanocomposite layers.

E-mail address: csari86@gmail.com (I. Csarnovics).

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2. Experimental details

2.1. Organic materials

The next materials and chemicals were used in this work: Diurethane dimethacrylate, mixture of isomers (436909 Aldrich, UDMA), Isodecyl acrylate (408956 ALDRICH, IDA), Dodecanethiol functionalized gold nanoparticles, 3–5 nm (Nanoprobes, No. 3014, AuNPs), SiO_2 nanoparticles (S5505, nanoparticle size of 14 nm, SiO_2NPs), and 2.2-Dimethoxy-2-phenylacetophenone (initiator of polymerization, 19611-8 Aldrich, In2).

2.2. Preparation of organic nanocomposites

Two different systems were investigated in the framework of the same physical rout. The first was based on pure monomer UDMA, to which the AuNPs were added in the form of solution in toluene. The second contains the monomers with SiO_2NP to which AuNPs were added in the form of solution in toluene.

The compositions of the AuNP–SiO_2NP-monomer composites are presented in Table 1. They were prepared in the next way. Silicon oxide nanoparticles were added to the abovementioned monomers and the homogeneous solution was prepared by intensive stirring. A solution of AuNPs in toluene and initiator was added to this solution. Toluene was used for homogenization and later vaporized. Thick nanocomposite layers were formed on a glass substrate in the gap between the glass and a polyester film. The thickness of the layer was 60 μm. After a series of experiments the composition with 10 wt.% of SiO_2NPs and 0.15 wt.% of AuNPs was selected as the best for recording gratings with high efficiency, homogeneity and low scattering level.

2.3. Amorphous chalcogenide nanocomposite layers

Vacuum thermal evaporation–co-deposition of chalcogenide glass and gold onto the selected substrate, with further annealing to aggregate AuNPs can be used for the introduction of AuNPs to the chalcogenide glass matrix [6]. But this method can be applied only for the glasses with high softening temperatures, like $Ge_{20}As_{20}S_{80}$ ($T_g \approx 570$ K), which allows annealing of the layers at temperatures where the diffusion of Au atoms appeared sufficient for nano-clustering in the glass matrix.

In our present work we used glasses from the As–Se system with comparatively low softening temperatures (370–450 K), so the AuNPs with a radius between 30 and 90 nm were preformed on a silica glass substrate by annealing and Ostwald ripening of few nanometer thin gold layers, previously deposited on this substrate. These nanoparticles were covered by the layer of As–Se glass, thermally evaporated in vacuum, which thickness was 600 nm.

Holographic gratings (HGs) with a period of 2 μm were recorded in layers with and without AuNPs, by 325 nm radiation of He–Cd laser (100 mW) for polymers and 633 nm radiation of He–Ne laser (25 mW) for chalcogenides. The recording was performed with two p-polarized beams, each 12 mW, no additional illumination during recording was used for organic and chalcogenide layers in these experiments. Laser diode with emission at 532 nm (14 mW) was used for localized plasmon excitation in polymer nanocomposites for test of its influence on the polymerization process, but not yet during grating recording. The resulting nanocomposites and recorded holographic gratings (HGs) were characterized by a transmission electron microscope (TEM) (JEM-2000FXII), Hitachi scanning electron microscope (SEM), and atomic force-microscope (AFM) (Veeco di Caliber), and optical spectra were measured with a Shimadzu 3600 UV/VIS spectrometer. Diffraction efficiency DE of the recorded gratings was measured in transmission mode, at a normal incidence of 633 nm, and 12 mW laser beam polarized along the grating vector, with a statistical error of about 5% of the average value of DE for the given sample. The errors of the heights of the surface reliefs measured by AFM were not more as 10%.

Table 1
AuNP–SiO_2NP monomer compositions.

Type of the monomer	SiO_2NP [wt.%]	AuNPs [wt.%]	Initiator [wt.%]
UDMA	10	0.1–0.55	0.5
30 wt.% UDMA/70 wt.% IDA	10	0.08–0.3	0.5

3. Results and discussions

In our experiments the first and simple criterion of gold-containing nanocomposite formation was the presence of plasmon resonance peak in the optical transmission spectrum, which supports the separation of AuNP of given dimensions and proper resonance maximum. Plasmon resonance was not observed in optical transmission spectra for the AuNPs–polymer nanocomposites, where toluene was used for homogenization and later vaporized. The introduction of AuNPs just resulted their falling in sediment, caused by the agglomeration of nanoparticles.

According to our assumptions the introduction of SiO_2NPs should have a double role: to improve the contrast between the fringes of the recorded spatial reliefs as well as to improve the compatibility of AuNPs with organic matrix, which in turn will increase the efficiency of recording and the resulting contrast. Therefore monomer compositions with SiO_2NPs were prepared (Table 1). Monomer compositions and thick polymer films, which were obtained after UV-curing, were uniform and had pink-red color and low light scattering level. Absorption peaks were observed in 520–530 nm range for the monomer solution and in the polymer film (Fig. 1a), i.e. green illumination can excite localized plasmons in these nanocomposites. As it is shown on Fig. 1b the sizes of the AuNPs were about 5 nm, similar to the original gold nanopowder, and they were not agglomerated in the nanocomposite structure. The similar plasmon resonance absorption was observed in the investigated amorphous chalcogenide–AuNP nanocomposite structures (see Fig. 1c), in accordance with a previous data presented in [4].

The UDMA/0.15 wt.% AuNP/10 wt.% SiO_2NP and UDMA/IDA/10 wt.% SiO_2NP/0.15 wt.% AuNP nanocomposite samples as well as the same without AuNPs were used as light-sensitive media for recording holographic diffraction gratings.

The mechanism of grating recording based on monomer nanocomposites was proposed [7] and is as follows. Polymerization leads to the formation of chains of monomers in the bright regions during non-uniform illumination of monomer nanocomposite. This process lowers the chemical potential of monomers in the bright regions, leading to diffusion of monomers from the dark to the bright regions. Inorganic nanoparticles diffuse from the bright to the dark regions, since the particles are not consumed and their chemical potential increases in the bright regions. This process of mutual diffusion continues until the monomers are not used at all or until the high viscosity of the environment will not make the monomer molecules and the nanoparticles immobile. The spatial distribution of nanoparticles is fixed and a refractive-index relief as well as the surface relief of grating is created as a result of compositional and density differences between the bright and the dark regions. Thus, the redistribution of nanoparticles and monomers depends on the rate of polymerization and on the diffusion process of the monomers and nanoparticles. In our experiments sinusoidal interference pattern with a 2 μm period was projected to the surface of the layer and HG with redistributed amount of nanoparticles in valleys and ridges was recorded (see Fig. 2a). The redistribution of SiO_2NP (diffusion of nanoparticles out of illuminated fringes) was stimulated by the gradient of light intensities and degree of polymerization. It was observed, that the recording was enhanced at the presence of AuNPs, that indicates some influence of AuNPs on the abovementioned processes of polymerization and mass transport.