

Polymer Diffraction Gratings Modified with Silver Nanoparticles

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In the present research we have modified polymer gratings with silver nanoparticles deposited from colloidal solutions. Silver colloids were produced by chemical reduction of silver salt (silver nitrate AgNO_3) solution using different components. We have chosen two different preparation methods: modified Volski method – Ag1 (we have modified it) and Lee and Meisel – Ag2. UV-VIS spectrometry was used to control formation of nanoparticles in colloids. Comparison of theoretical (Mie light scattering theory) and experimental results showed that the diameter of silver nanoparticles in colloidal solution varies in the range 50 nm – 100 nm. The polymer 4 μm period grating was formed by replication of silica matrix by photopolymer and using UV hardening of the structure. The modification with silver nanoparticles was performed using a dip – coating technique. Dipping was performed for 72 hours in two solutions separately. Analysis of modified structures was performed with UV-VIS spectroscopy, atomic force microscope (AFM) and scanning electron microscope (SEM). Optical properties of diffraction grating before and after modification were investigated measuring diffraction efficiency. The diffraction efficiency was measured using three wavelengths: He-Ne ($\lambda = 632.8$ nm), DPSS ($\lambda = 532$ nm), He-Cd ($\lambda = 441.6$ nm). It was found that using different colloidal solutions it is possible selective deposition of the nanoparticles. AFM and SEM results indicate that silver nanoparticles from the solution Ag1 were assembling on the grooves of the grating whereas particles from the solution Ag2 were assembling in the valleys of the grating. Resonant plasmonic response of the grating/silver nanoparticles system enabled to control diffraction efficiency of the final grating.

Keywords: silver nanoparticles, replication of periodic structure, self assembly.

1. INTRODUCTION

The assembly of anisotropic metal nanoparticles on planar surfaces still requires more sophisticated methods such as lithography. K. Aslan [1] reported the growth of silver nanorods directly on glass substrates on the solution-seeded nanorod synthesis scheme. This new approach enables one to control the size/loading density of the silver nanorods on the glass substrates by controlling simple experimental parameters such as immersion time, concentration, temperature, and the surfactant. These advances are directed at fabricating new quick and cheap silvered surface for applications in metal-enhanced fluorescence based clinical assays and in drug discovery [2 – 4]. Primarily quartz or glass substrates with deposited silver nanostructures have been used. This has been caused by the reason that chemistries of the surface of glass (and quartz) are well established and therefore the covalent immobilization of silver nanostructures onto glass is less arduous and is reproducibly reliable. Polymeric substrates may, however, provide a suitable cheap and versatile alternative to the use of chemically benign glass substrates. Although often unsuitable for short wavelength fluorescence-based detection strategies due to intrinsic polymer fluorescence, several polymers, such as poly(methyl methacrylate) and polycarbonate (PC), typically do not suffer from these detractors and are suitable

for use in longer-wavelength ($\lambda > 520$ nm) fluorescence-based detection schemes [5].

Polymeric substrates can be used as substrates for metal-enhanced fluorescence, which, given their cost, are likely to be much better received by industry. While hydrophilic polymers are already available with a high surface density of either hydroxyl or amine groups, they are used for silver deposition. Plastics with a low density of surface functionality could be surface modified. The optical density of silver nanorods on polymer as polycarbonate (PC) and on glass substrates were around 0.3. Plasmon absorption band for the silver nanorods was also found to be slightly red-shifted on the PC film as compared to that typically observed on glass substrates [1, 2].

The diffraction efficiency of the grating depends strongly on the concentration of the nanoparticles. Maximum diffraction efficiencies of holographic gratings, recorded with nanosecond pulses in samples of different volume fractions of silver nanoparticles in colloidal solution, were around 3 % [6].

We present a new method of modification of periodical polymer based micro structures with silver nanoparticles.

2. EXPERIMENTAL

2.1. Formation of periodical structures

The diffraction grating was produced in the main technological steps such as origination (based on microlithography and dry etching), replication and UV

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hardening. The master matrix microstructures were produced in silica. PET was used (25 μm thick made by Vladimir Chemical Group of Enterprises) as a substrate for polymer periodical structure. The PET substrate before replication was exposed to plasma treatment using gaseous plasma of oxygen and nitrogen for 90 s as described in [7].

UV light hardening layer was formed using commercial photopolymer (acrylic trimethylolpropane ethoxylate) (layer thickness 2 μm , area 3 cm^2), PET substrate and UV lamp ($T = 20\text{ }^\circ\text{C}$, irradiation distance 10 cm, UV light source DRT-230: $\lambda = 360\text{ nm}$, $I = 10\text{ klx}$).

The periodic structure (period 4 μm) was produced directly making a polymer replica by sandwiching UV-photopolymer between the silica structure stamp and a plasma treated PET. After 50 s of UV exposure a uniform layer was obtained and the silica stamp was removed [8].

2.2. Formation of silver colloids

In this experiment two colloidal solutions were made according to different preparation techniques.

The first colloidal solution (Ag1) was made according to P. Volski preparation technique, which we have modified. In a typical experiment, 2 ml of 17 % silver nitrate (AgNO_3), 0.2 ml of 0.25 % gelatin and 1 ml of 0.001 N hydroquinone $\text{C}_6\text{H}_4(\text{OH})_2$ were added to 30 ml of distilled water. The pH of solution was 9.8.

The second silver colloidal solution (Ag2) was prepared using a chemical reduction method according to the description of Lee and Meisel [9]. All solutions of reacting materials were prepared in distilled water. In a typical experiment 90 mg of AgNO_3 were added to 500 ml of distilled water. The solution was heated until boiling temperature. 2 ml of 1 % trisodium citrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$) was added drop by drop to this solution. During the process, solution was mixed vigorously. Solution was heated for 60 minutes (until colour change is evident (pale yellow)).

2.3. Modification of periodic structures with silver nanoparticles

Deposition of silver nanoparticles was performed in a Langmuir-Blodgett trough (Microtestmachines Co, Belarus), in a dipper unit. The substrates were vertically dipped into silver colloidal solutions (two samples in two different solutions), pulled down and left in the solution for 72 hours. After this time the samples were pulled out and dried in room temperature at ambient pressure keeping pressed between two plates of fluoroplast.

2.4. Analysis techniques

The optical properties (absorbance) of colloidal solutions and samples were evaluated with UV/VIS/NIR spectrometer (Avantes-2048) with a light source – combined deuterium-halogen lamp (AvaSpec-Dhc) and spectral range: 200 nm – 1100 nm.

Morphology of the structures was investigated with an atomic force microscope (NANOTOP–206) operating in a contact mode (cantilever force constant 3 N/m) and field emission scanning electron microscope Hitachi S-4800 (voltage in the range 0.5 kV – 30 kV, resolution of 1 nm).

Image processing and analysis of the AFM data was performed with a program “Surface View version 2.0”.

Diffraction spectra were registered with the diffraction stand. Three lasers at different wavelengths (He-Ne [$\lambda = 632.8\text{ nm}$], DPSS [$\lambda = 532\text{ nm}$], He-Cd [$\lambda = 441.6\text{ nm}$]) and a photodiode were employed.

3. RESULTS AND DISCUSSIONS

3.1. Optical properties of colloidal solutions and samples

UV-VIS absorption spectroscopy have been proved to be quite sensitive to the formation of silver colloids because silver nanoparticles exhibit an intense absorption peak due to the surface plasmon (it describes the collective excitation of conduction electrons in a metal) excitation [11]. The UV-VIS spectra of both colloids (Ag1 and Ag2) are shown in Fig. 1, a). The surface plasmon related Peaks are localised around 425 nm – 430 nm wavelength indicating similar lineas dimensions of the nanoparticles. The absorbance of solution Ag1 is about 3 times larger than the absorbance of solution Ag2. It indicates that the concentration of silver nanoparticles is higher in solution Ag1.

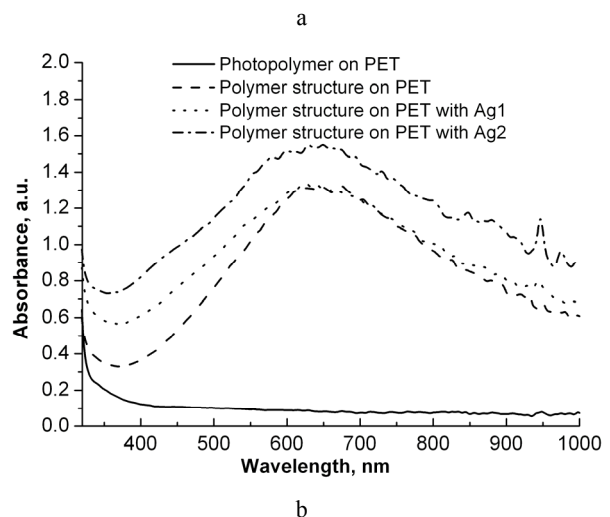
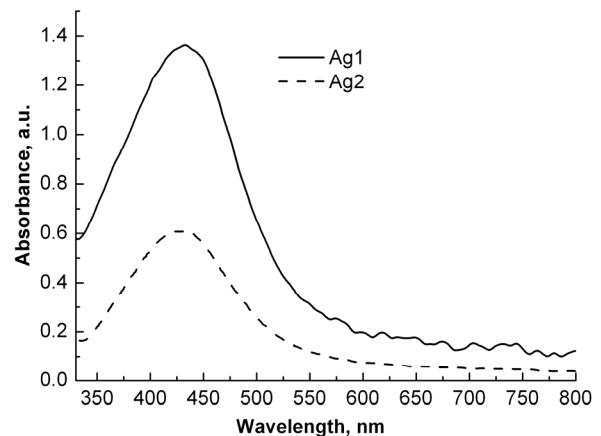


Fig. 1. UV-VIS spectra: a – of colloidal solutions; b – of periodic structures before and after modification

To determine the particle size in the solutions we performed several calculations with computer simulation program “MiePlot v. 3.4” [10] as described in [11]. Theo-

retical calculations predicted that the size of particles in the solutions with small variation (about 10 %) is around 50 nm.

According to Aslan [1] the simple adsorption of silver nanorods to the glass slides from the solution took several days and absorption reached only 20 % that of the silver nanorods in solutions. As indication of formation of colloidal solution is the colour change – in the same manner we can describe the periodic structures after the modification. The colour of the polymer structure has changed after modification with silver nanoparticles. Structure dipped in a colloidal solution Ag1 became brown with brown spots, whereas structure dipped in a solution Ag2 became yellow. Independently of the colour change the periodic structure remained stable on the PET substrate, that was proved by white light dispersion from the grating. For more detail quantitative examination of the change of optical properties UV-VIS spectroscopy was used (see Fig. 1, b).

In Fig. 1, b, one can see the initial optical spectra of the polymer substrate, polymeric grating before modification and of the gratings after modification with the silver nanoparticles solutions. One can clearly see that the

absorption peak of the produced phase grating is situated at ~650 nm. After the surface modification with silver nanoparticles the position of the peak doesn't change, but the shape (width) of the peak was changed. The absorption intensity of the diffraction grating modified with a solution Ag1 didn't change, whereas the intensity of absorption peak of the grating modified with a solution Ag2 has increased about 0.4 a.u (~33 %). This absorption signal enhancement could be attributed to the interaction of the surface plasmons with incident light due to absorption of silver nanoparticles from the colloidal solution.

3.2. Morphology of periodic structures

The AFM pictures of periodic structures are shown in Fig. 2. One can see three different topography pictures of three gratings (a – reference grating, c – grating modified with a solution Ag1, e – grating modified with a solution Ag2). Statistical analysis of the photographs has shown that the roughness parameters of the grating have changed after the modification. Statistical parameters are summarised in Table 1.

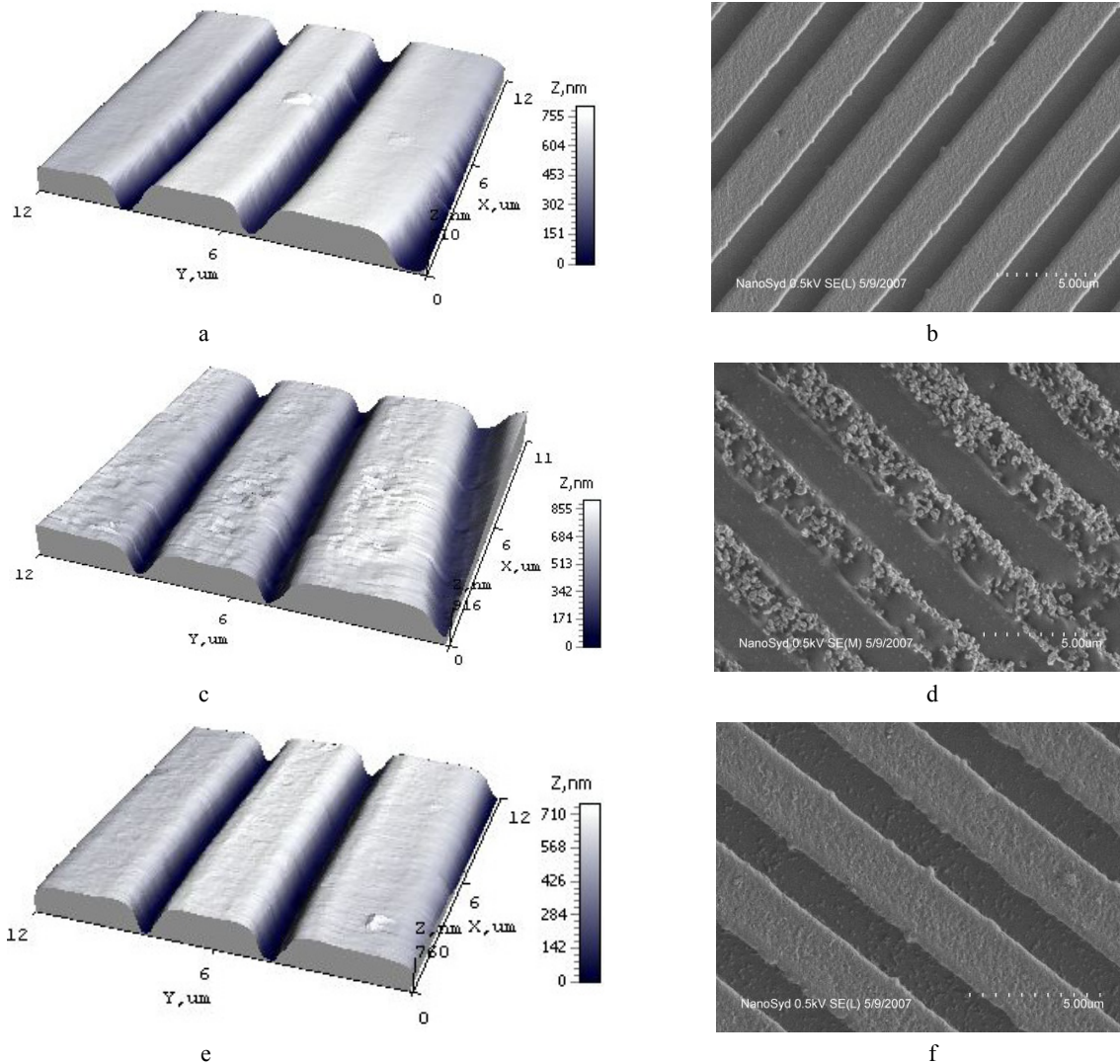


Fig. 2. AFM and SEM views of periodic structures before and after modification: a, c, d – topographical images of unmodified polymer grating, modified with silver solution Ag1, modified with silver solution Ag2 respectively; b, d, f – SEM pictures of diffraction grating before modification, modified with colloidal solution Ag1, modified with colloidal solution Ag2 respectively

Table 1. Statistical parameters of periodic structures in polymer

| Sample | R_a , nm | R_q , nm | Z , nm |
|-------------------|------------|------------|----------|
| Polymer grating | 168.3 | 217.9 | 540.0 |
| Modified with Ag1 | 177.3 | 221.1 | 704.6 |
| Modified with Ag2 | 146.7 | 195.3 | 506.0 |

Abbreviations: Z – maximum height, R_a – roughness average, R_q – root mean square roughness.

From the roughness parameters one can see that for the grating modified with the silver solution Ag1 roughness has increased. This indicates about self assembly of silver nanoparticles on the grooves of polymeric grating. In the case of silver solution Ag2 one can see opposite change – roughness parameters became smaller. It indicates about self assembly of silver nanoparticles in the valley of the grating. The same predictions could be made if we would take height differences in account.

The SEM pictures have proved directly the prediction for the solution Ag1. From the SEM pictures, one can see that nanoparticles are situated on the grooves of the grating (see Fig. 2, d) for this grating. The size of nanoparticles defined from the photo on the grating varied from 50 nm to several hundred nanometers. For the other grating (modified with solution Ag2) assembly of silver nanoparticles is not so visible. In the Fig. 2, f, one can see qualitative changes of the surface comparing with the initial grating (see Fig. 2, b) and these changes are more pronounced in the valleys of the grating.

3.3. Diffraction efficiency of periodic structures

The quantitative influence of the modification on the diffraction grating properties was evaluated measuring the diffraction efficiency of the initial diffraction grating and modified grating. The results for three wavelengths are presented in Fig. 3.

One can see in Fig. 3, a, that both gratings act differently: diffraction efficiency of the grating modified in the solution Ag1 increases fractionally and for the grating modified in the solution Ag2 decreases for the zeroth diffraction maxima; in the first diffraction maxima diffraction efficiency of the grating modified in the solution Ag1 doesn't change and increases for the grating modified in the solution Ag2. For other wavelengths response from the gratings is more pronounced (see Fig. 3, b and c). One can see in Fig. 3, b, that in the zeroth order diffraction maxima diffraction efficiency of both modified gratings increases differently – diffraction efficiency for the grating modified in solution Ag1 is higher. In the first diffraction maxima response of the gratings is opposite – diffraction efficiency decreases and this time the decrease is higher for the grating modified with the solution Ag1. In the third diffraction maxima response of the gratings is similar to the zeroth order diffraction maxima (diffraction efficiency has increased for both gratings). For the wavelength of $\lambda = 632.8$ nm the diffraction efficiency in the zeroth and second order diffraction maxima decreased for both gratings modified in different solutions. In the first order the diffraction efficiency has increased for both

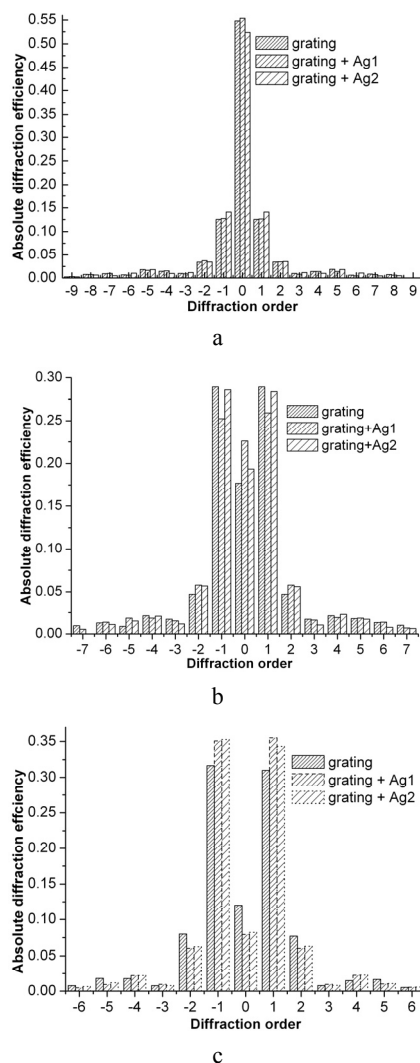


Fig. 3. Absolute diffraction efficiency of polymer periodic structures before and after modification for the wavelengths: a – $\lambda = 441.6$ nm, b – $\lambda = 532$ nm, c – $\lambda = 632.8$ nm

gratings. The enhancement of the signal possibly could be attributed to the surface plasmon resonance at the surface of silver nanoparticles.

4. CONCLUSIONS

UV-VIS absorption results confirmed formation of the silver nanoparticles prepared in liquids by chemical reduction method. We have performed deposition of silver nanoparticles using dip-coating method. Results of UV-VIS spectroscopy have confirmed self assembly of silver nanoparticles on diffraction gratings.

From the AFM and SEM measurements we could make an assumption that silver nanoparticles from different solutions assemble differently on the surface: particles from the solution Ag1 (modified Volski) assemble on the grooves of the grating and particles from the solution Ag2 (Lee and Meisel technique) assemble in the valleys.

Investigation of diffraction efficiency of the grating has shown that for the wavelengths of $\lambda = 532$ nm and $\lambda = 632.8$ nm the efficiency has been changed after modification. Diffraction efficiency of the grating has increased in zeroth and decreased in first diffraction

maxima for the wavelength of $\lambda = 532$ nm. For the wavelength of $\lambda = 632.8$ nm diffraction grating response is opposite – diffraction efficiency decreases in zeroth and increases in the first diffraction maxima. This could be explained by surface plasmon resonance at the surface of silver nanoparticles. The response of the gratings depends on the size of nanoparticles on the gratings and it is stimulated differently for different wavelengths ($\lambda = 532$ nm and $\lambda = 632.8$ nm). Response on the shortest wavelength ($\lambda = 532$ nm) is not so pronounced.

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