



Photoresist modification by silver colloid solution: the role of silver nanoparticles content

Jovita Pudlauskaitė^{a*}, Igoris Prosyčėvas^b, Virginija Jankauskaitė^a, and Tadas Kleveckas^a

^a Faculty of Design and Technologies, Kaunas University of Technology, Studentų g. 56, Kaunas, LT-51424, Lithuania

^b Institute of Materials Science, Kaunas University of Technology, Savanorių pr. 271, Kaunas, LT-50131, Lithuania

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Abstract. The aim of this work was to investigate the influence of silver nanoparticles deposited from a colloid solution into a photoresist composition on the morphology and optical properties of the grating. The Ag colloid was produced by chemical reduction of silver nitrate and incorporated in the photoresist composition by mixing. The film of Ag colloid solution modified photoresist was obtained by spin coating on an optical quartz substrate and dried at 100 °C for 20 min. The grating with a period of 4 μm was formed by contact lithography.

The synthesized Ag nanoparticles were spherical or roughly spherical with diameters varying from 10 nm up to 60 nm. The content of Ag nanoparticles in the photoresist rose from 0.02 wt% to 4.66 wt% when the concentration of the Ag colloid solution increased from 10 to 30 wt%.

Analysis performed with atomic force microscope and scanning electron microscope showed that Ag nanoparticles changed geometrical parameters and optical properties of the gratings: their height decreased and diffraction efficiency increased in all orders. However, the increase of the Ag content up to 4.66 wt% considerably changed the grating geometry. In this case the ridges of the grating became concave, probably due to the Ag nanoparticles light diffusion. For this reason secondary reflections appeared during photolithography and the ridge of grating is affected by exposure. Therefore the ridge surface becomes soluble to etching solvents, and exposure areas are removed.

Key words: photoresist, silver nanoparticles, grating, surface morphology, diffraction efficiency.

INTRODUCTION

Photopolymers are the most promising material for the formation of diffraction gratings with good mechanical properties and chemical resistance. They have numerous advantages for this, such as simple preparation, self-developing capability, response for visible light, high diffraction efficiency and hardening speed, and energetic sensitivity. However, nowadays technologies are continuously requiring new materials with special combinations of exclusive properties. Therefore, investigations of polymer and metal particles nanocomposites have received considerable interest due to their unique properties [1,2].

Nanoparticles such as Ag, Au, and Cu are of interest because of their chemical and physical properties. These

metal particles display surface plasmon resonance in the visible spectrum region. Ag exhibits the highest efficiency of plasmon excitation. Moreover, optical excitation of plasmon resonance in nanosized Ag particles is the most efficient mechanism by which light interacts with material [3]. By combining features of polymer with Ag nanoparticles it is possible to expand application fields, to open ways to a new generation of materials with unique electrical, optical, or mechanical properties, and to make them attractive in areas like photoimaging and patterning, optics, sensor design, catalysis, and antimicrobial coatings [4–7].

Polymer–metal nanocomposites can be prepared by different methods including polymerization, solid state polymer transformation, sol–gel synthesis, mixing, etc. [8–10]. On the other hand, metal nanoparticles can be deposited on the surface of the polymer layer by spraying, ultrasound-assisted, and dipping methods [11,12].

* Corresponding author, j.pudlauskaite@yahoo.com

The properties of the nanocomposite are related to several factors such as the filler nature and concentration, polymer matrix dimension, and morphology of the filled materials [7].

It is possible to control the position of the Ag nanoparticles when polymer surface modification is performed by the dip-coating method. In [12] it was determined that nanoparticles from a solution obtained by the Volski method assemble on the grooves, while nanoparticles from a solution prepared by the Lee–Meisel method assemble on the valleys. Both these polymer modification methods improve optical properties of the photopolymer grating surface, but the Lee–Meisel method is more efficient.

Although a large number of polymer modification processes were reported in [8–14], the effect of the Ag content on the properties of the grating has not been widely studied. Therefore, the goal of this work was to create a diffraction grating with new properties by the modification of photoresist with Ag nanoparticles prepared by the Lee–Meisel method and to investigate the influence of the nanoparticles content on the morphology and optical properties of the grating.

EXPERIMENTAL

Materials

The Ag colloid solution was prepared using the chemical reduction method according to the description of Lee and Meisel [15]. AgNO_3 (Sigma Aldrich, UK) was added to distilled water and the solution of 0.05% concentration was heated until boiling temperature. To this solution 2 mL of 1% trisodium citrate $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$ (Sigma Aldrich, UK) was added drop by drop and mixed. After 60 min heating the Ag colloid solution was stirred until it cooled down to room temperature.

UV-curable compositions of different concentration consisting of positive tone photoresist ma-P 1225 (Micro Resist, Germany) and Ag colloid were prepared. The grating with 4 μm period was formed by contact lithography. A mask was placed on the photoresist to expose a particular periodic pattern within the material. The UV exposure intensity was 55 mJ/cm^2 ($\lambda = 365$ nm), and the time of exposure was 10 s. The wafer was rinsed in a developing solution (ma-D 331) to remove the exposure areas of the photoresist. The photoresist layer was coated on an optical quartz surface. Before coating the substrate was cleaned chemically to remove organic contaminants and dried in a clean air laminar flow workstation. The film of photoresist was obtained by the spin coating technique using a centrifuge “Dynapert Precima” (Colchester, UK). The coating was performed at 30 s rotation speed of 2500 min^{-1} and then dried for 20 min in a convection

oven at 100 °C temperature. A film of 2.5 μm thickness was obtained.

Characterization methods

The optical properties (absorbance) of the Ag colloid solution and modified photoresist were evaluated by ultraviolet–visible light spectrometry (UV–VIS) using a spectrometer Avantes-2048 with the spectral range of 200–800 nm.

Scanning electron microscope (SEM) JSM-IC25S (JEOL, Japan) was used for colloidal particle imaging. For investigation the solution drops were deposited on a silicon wafer and dried at ambient temperature.

The surface topography of gratings was studied from images obtained by SEM FEI Quanta 200 FEG. The samples were examined in low vacuum mode operating at 20.0 kV using an LDF detector. The content of Ag nanoparticles and chemical analysis of the grating were performed by the energy dispersive X-ray analyser SEM/EDX technique with a Bruker XFlash 4030 detector (FEI, USA) (accelerating voltage 10 kV, distance between the bottom of the objective lens and the object 10 mm).

An atomic force microscope (AFM) (NT-206; Microtestmachines Co.) using SPM processing software *SurfaceView* was applied to investigate grating morphology and geometry. The topographical images were collected in air at room temperature using a V-shaped silicon console operating in the contact scanning mode with 15 $\mu\text{m} \times 15 \mu\text{m}$ field-of-view and scanning speed of 10 $\mu\text{m}/\text{s}$. Surface roughness was evaluated by the statistical parameters average roughness R_a , root-mean-square roughness R_q , and mean height of the grating H_{mean} .

Diffraction efficiency of the grating was measured experimentally by He–Ne laser with a wavelength of $\lambda = 632.8$ nm. The relative diffraction efficiency was defined as the ratio of the particular wavelength intensity of the light transmission through the grating in the given diffraction orders $I(\theta)$ and the intensity of the laser $I(0)$.

RESULTS AND DISCUSSION

Characterization of silver nanoparticles

The absorption band in the visible light region of 350–550 nm is typical of Ag nanoparticles, because Ag nanoparticles exhibit an intense absorption peak due to the surface plasmon excitation (Fig. 1, curve 1). According to the Mie theory, the position and shape of the plasmon absorption depend on the particle size and shape and the dielectric constant of the surrounding medium [16]. In the Ag colloid spectrum one symmetric

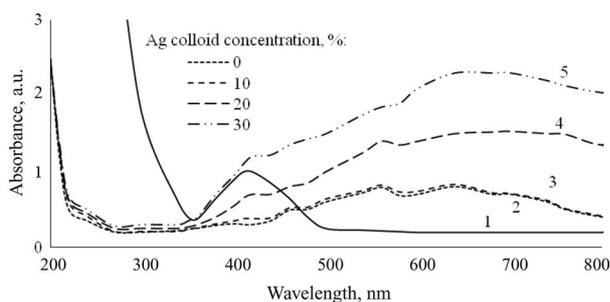


Fig. 1. The UV–VIS absorption spectra of Ag colloid (1) and photoresist unmodified (2) and modified with Ag colloid of different concentrations (3–5).

absorption peak at around 420 nm is visible. It is characteristic of small (20–30 nm diameter) and spherical or roughly spherical Ag nanoparticles [17,18].

It is evident that the absorption spectrum of the photoresist with 10% Ag colloid is similar at the unmodified grating and has no changes in the part of the spectra characteristic for Ag nanoparticles (Fig. 1, curves 2, 3). The absence of peak could be explained by the low Ag concentration in the photoresist. At a higher Ag colloid concentration (20%) a small peak appears at 420 nm, attributed to the Ag ions. Further increase of the Ag colloid up to 30% increases the absorbance peak in the 370–800 nm range about two times compared with that at 20% colloid concentration. It could be attributed to the interaction of the plasmons with incident light due to the absorption of Ag nanoparticles from the colloid solution.

The shape, diameter, and size distribution of the Ag nanoparticles were determined and measured by analysing a SEM picture of the Ag colloid. In Fig. 2a small grains and separate nanoparticles are visible. Some of the Ag nanoparticles tend to stick and form large agglomerates (50–300 nm) due to their high surface energy. For the evaluation of the Ag nanoparticles distribution the agglomerates larger than 60 nm were eliminated. The obtained histogram of the nanoparticles size distribution is presented in Fig. 2b. It is evident that the diameters of the Ag nanoparticles vary in a wide range, from 10 to 60 nm, but nanoparticles with diameters of 25–30 nm dominate in the colloid solution. This can explain the broad UV–VIS absorption peak in the absorption spectra of the colloid (Fig. 1, curve 1). Thus, the nanoparticles size determined from the absorption spectra correlates roughly with that determined from the SEM photograph.

The standard EDX spectrum recorded on the photoresist modified with the Ag colloid solution of 20% concentration is shown in Fig. 3. As can be seen, various elements are detected on the grating surface, i.e. C (~45 wt%), Si (~16 wt%), O (~28 wt%), P (0.44 wt%), Zn (0.59 wt%), and Ca (3.4 wt%). These elements can be attributed to the photoresist or to the

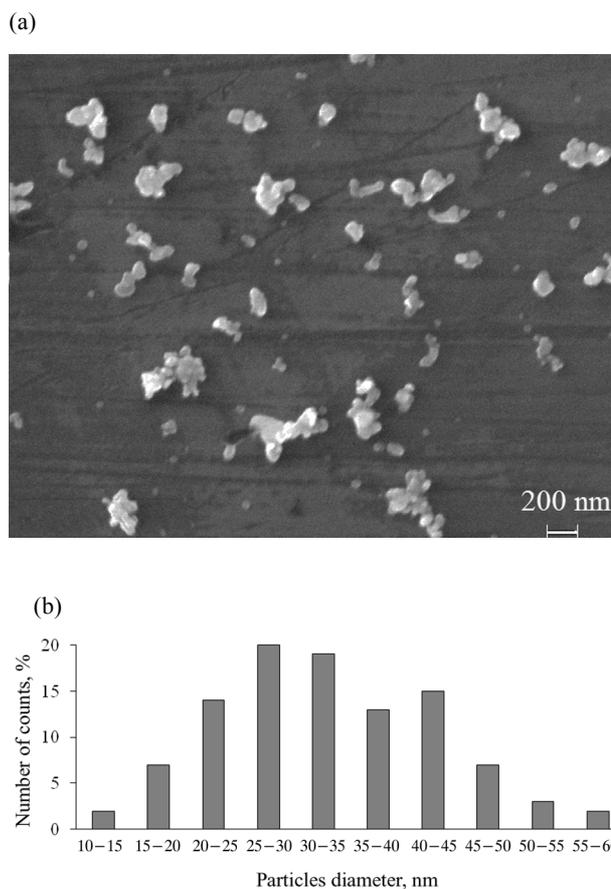


Fig. 2. SEM image of Ag colloid solution dried on the silicon: (a), image used for the determination of size distribution; (b), histogram of Ag nanoparticles size distribution.

glass that was used as substrate. The peaks located at 0.2 and 3 keV are directly related to the Ag characteristic lines K and L.

The influence of the concentration of the colloid solution on the content of Ag nanoparticles in the photoresist composition is shown in Fig. 4. At 10% Ag in the colloid solution the nanoparticles content is only 0.02 wt%, but it will increase about 14 times when the concentration of the Ag colloid solution increases up to 30%. In this case the Ag content reaches 4.66 wt%.

Morphology of grating

The SEM images of the surface of gratings are presented in Fig. 5. Comparison of the appearance of the grating before the incorporation of Ag nanoparticles (Fig. 5a) with gratings modified with Ag nanoparticles with a content of 0.02 and 0.33 wt% (Fig. 5b and c) shows no noticeable changes in the main parameters of the grating. However, quite a different grating surface morphology was obtained in the case of high Ag nanoparticles content (4.33 wt%): the shape of the grating

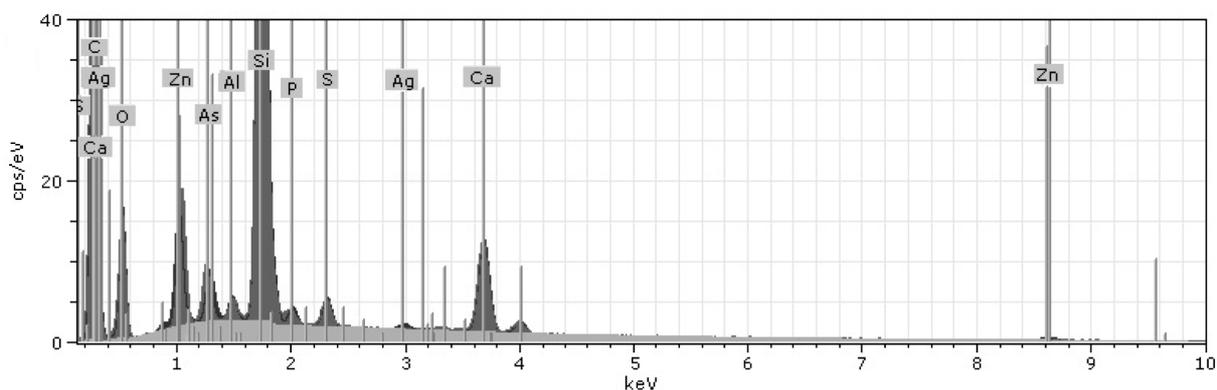


Fig. 3. EDX spectrum of the photoresist modified with 20% Ag colloid solution.

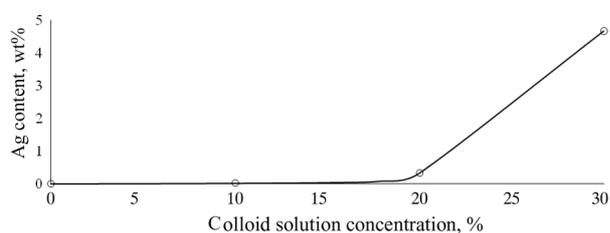


Fig. 4. Dependence of Ag nanoparticles content upon the concentration of the Ag colloid solution.

has considerably changed and its ridges have become concave (Fig. 5d).

AFM images and profilograms show these differences in the grating surfaces with different Ag nanoparticles content more clearly and accurately (Fig. 6 and Table 1). The values of the average roughness R_a and root-mean-square roughness R_q of gratings before the incorporation of Ag nanoparticles are masked (300 nm) because there is no deviation from the mean surface level. An increase of the grating period up to 4.6 μm is observed in the case of unmodified grating compared to the period of the mask (Fig. 6a). It may be related to the relaxation processes in the polymer layer. The increase of the Ag nanoparticles content decreases the surface roughness (R_a and R_q) and the height of the grating (more than 10 times). In this case the gratings period is still 4 μm , but the width of the ridges increases while the width of the grooves decreases.

Such alteration in the geometrical parameters may be related to the Ag nanoparticles light absorption. In this study small Ag nanoparticles (up to 50 nm) dominated. Such nanoparticles initiate higher light absorption than diffusion compared to the greater nanoparticles [19,20]. As was shown above, the increase of Ag nanoparticles content increases the absorption of light. Therefore, part of the light used for the formation of grating is absorbed by Ag nanoparticles. After contact lithography the unexposed photoresists become resistant to etching solvents, while exposed areas are

removed. However, the influence of light exposure on photoresists decreases due to Ag nanoparticles light absorption and part of the photoresist becomes solvent-resistant. As a result, the depth of the grating decreases and the width of the ridge increases.

Ag nanoparticles not only absorb but also diffuse light. For this reason at high Ag nanoparticles content secondary reflections appear during photolithography. They are supposed to influence the ridges surface. Therefore, the exposed photoresist becomes soluble to etching solvents and the ridge of the grating becomes concave at approximately 50% of the grating's height.

Diffraction efficiency of grating

The quantitative influence of the modification on the optical properties of the diffraction grating was evaluated by measuring the absolute diffraction efficiency (DE) of the gratings. DE shows the impact of the material composition on optical characteristics of the grating. Diffraction grating has low energy because it is made of photoresist modified with Ag nanoparticles. Therefore, the throughput of DE was evaluated in optical measurements.

Absolute DE is obtained by comparing the content of energy entering the i -th peak with the emitted laser energy. Our investigation showed that the Ag nanoparticles increase DE in all maximums (Fig. 7). The maximum DE (14%) in the first maximums was obtained in the photoresist with 0.33 wt% of Ag nanoparticles. In this case DE increased about 2.5 times compared to the photoresist without Ag nanoparticles. At 4.66 wt% of Ag DE in the first order was around 10%, but in the 0th order it doubled. At this content Ag nanoparticles exhibited the highest efficiency of plasmon excitation; therefore, an increase in the content of Ag nanoparticles changes the optical properties of the material and leads to the growth of light scattering. However, no increase of DE was observed in the first maximums. This means that changes in the DE can be attributed to the significant alteration of geometrical parameters of the grating's microrelief (Fig. 5d and Fig. 6d).

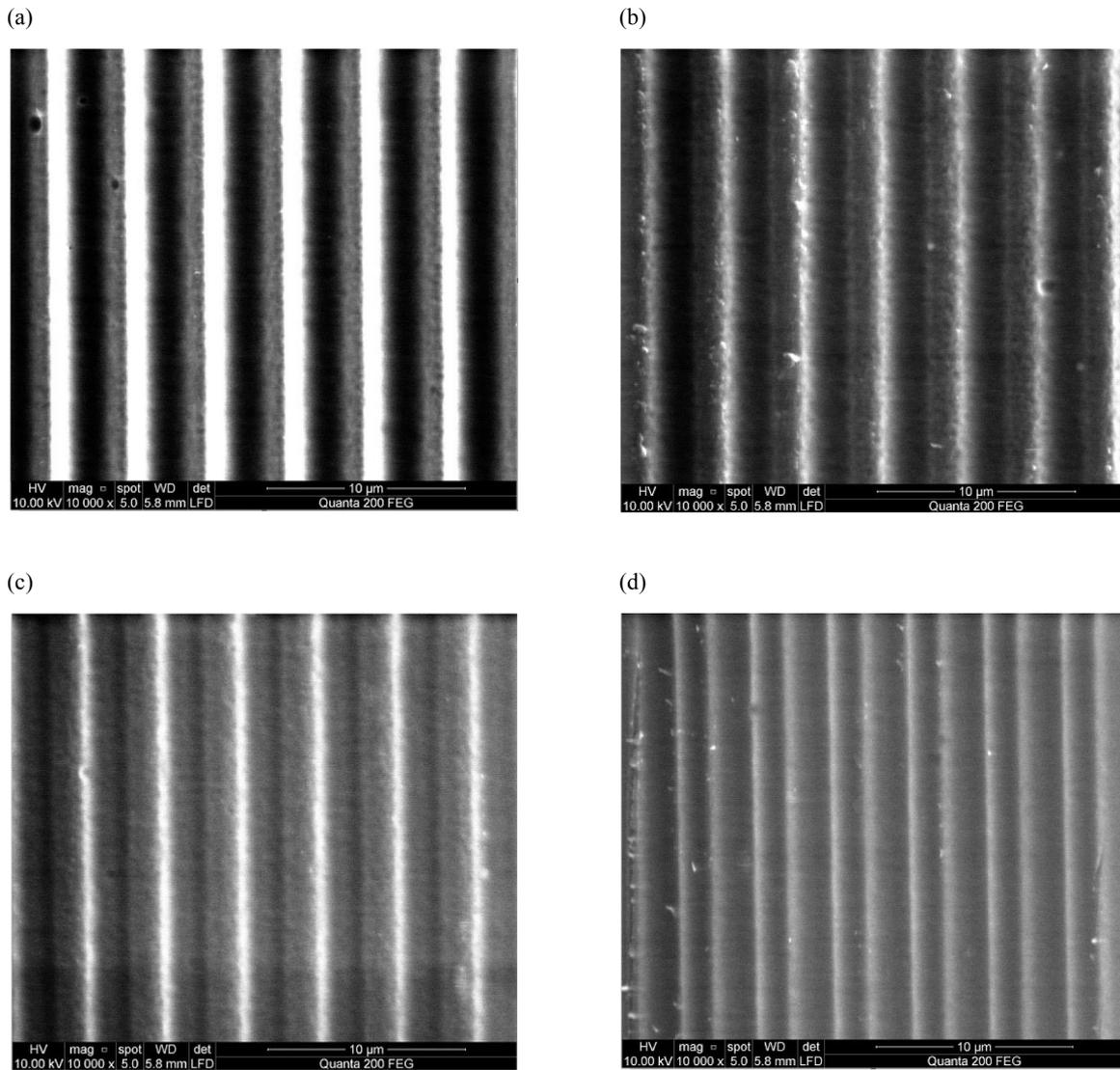


Fig. 5. SEM images ($\times 10\,000$) of grating depending on the Ag nanoparticles content, wt%: (a), 0; (b), 0.02; (c), 0.33; (d), 4.66.

Table 1. Influence of Ag nanoparticles on the geometrical parameters of the grating in photoresist

Content of Ag nanoparticles, wt%	Average roughness R_a , nm	Root-mean-square roughness R_q , nm	Height, nm	Mean height, nm	Width of ridge, μm	Width of groove, μm
0	300.0	300.0	1296	800	2	2.6
0.02	128.0	137.7	558	395	2.2	1.8
0.33	98.8	115.3	472	360	2.4	1.6
4.66	30.0	34.7	119	76	2.6	1.4

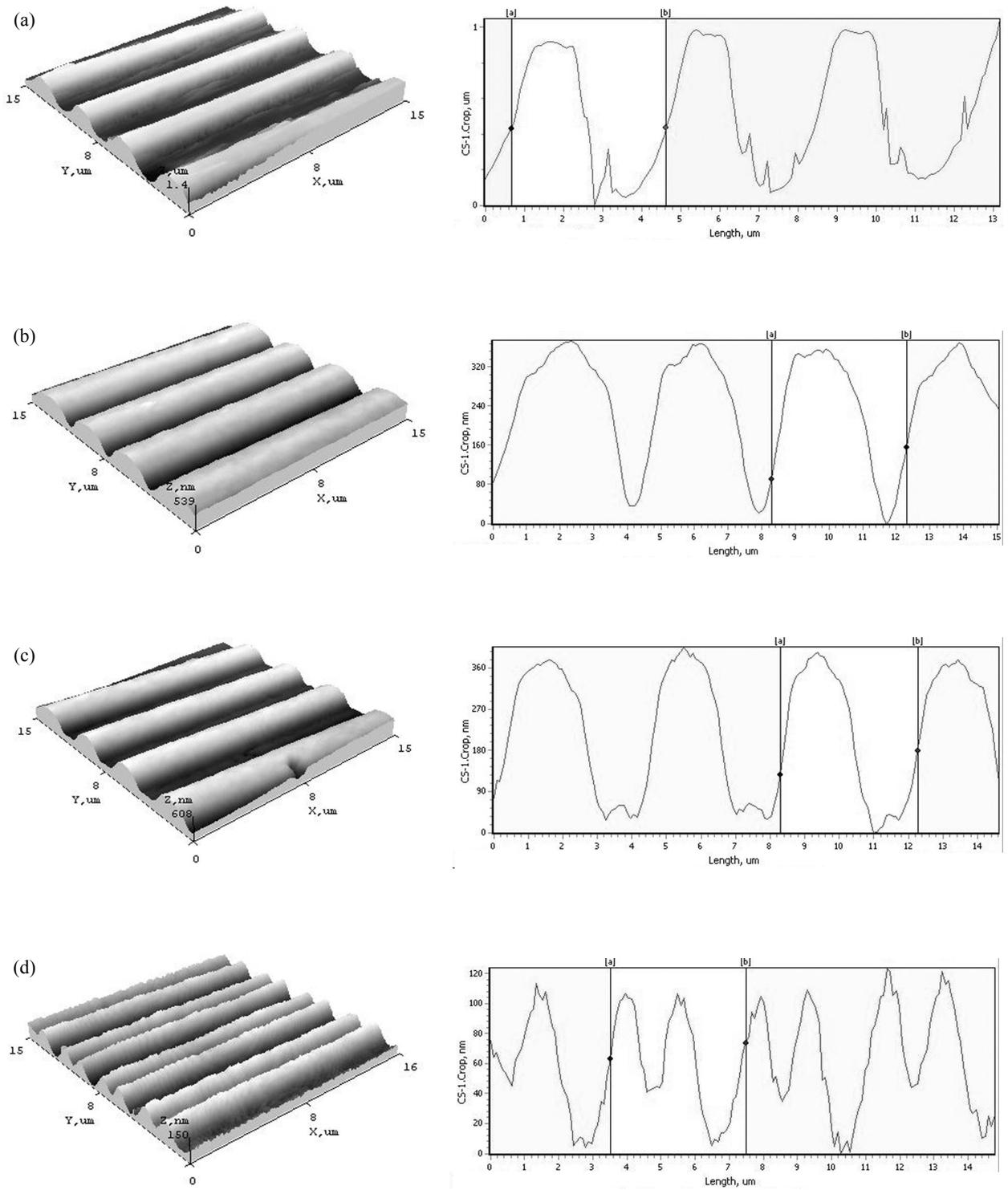


Fig. 6. AFM images and profilograms of grating depending on the Ag nanoparticles content, wt%: (a), 0; (b), 0.02; (c), 0.33; (d), 4.66.

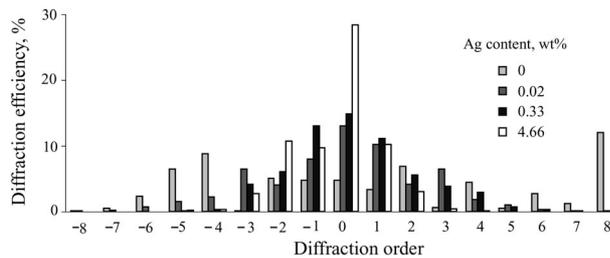


Fig. 7. Dependence of the diffraction efficiency of the periodic structure on the Ag nanoparticles content.

CONCLUSIONS

Incorporation of Ag nanoparticles obtained by the Lee–Meisel method in the photoresist composition changes the morphology and optical properties of diffraction grating. Increasing Ag content from 0.02 wt% up to 0.33 wt% decreases surface roughness, height of grating, and width of groove. High Ag content (4.66 wt%) changes the geometry of the grating and influences the appearance of ridges concavity due to the light diffusion by Ag nanoparticles.

Ag nanoparticles increase diffraction efficiency in all orders. The maximum diffraction efficiency in the first and zero orders was obtained in the photoresist with 0.33 wt% and 4.66 wt% of Ag nanoparticles.

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Fotoresisti modifitseerimine hõbeda kolloidlahuse abil: hõbeda nanoosakeste sisalduse tähtsus

Jovita Pudlauskaitė, Igoris Prosyčevas, Virginija Jankauskaitė ja Tadas Kleveckas

Uuriti hõbenitraadi taandamisest saadud kolloidlahusest sadestatud ja fotoresisti koostisesse segatud hõbeda nanoosakeste mõju difraktsioonivõre morfoloogiale ning optilistele omadustele. Hõbeda kolloidlahusega modifitseeritud fotoresisti kile kanti *spin coating*'u (tsentrifuugimise) teel optilisele kvartssubstraadile ja kuivatati 100°C juures 20 minutit. Kontaktlitograafiameetodil moodustati võre perioodiga 4 µm. Hõbedaosakesed olid jämedas lähenduses kerakujulised ja läbimõõduga 10–60 nm ning nende sisaldus fotoresistis varieerus 0,02-st 4,66 massiprotsendini, kui hõbeda kolloidlahuse kontsentratsioon suurenes 10-lt 30 massiprotsendini. AFM- ja SEM-analüüs näitasid, et hõbedaosakesed muudavad võrede geomeetrisi parameetreid ning optilisi omadusi: kõrgus vähenes ja difraktsiooni efektiivsus suurenes kõigis järkudes. Hõbeda kontsentratsiooni suurendamine 4,66 massiprotsendini muudab siiski oluliselt võre geomeetriat: võrejoonte harjad muutuvad nõrgusaks (arvatavasti valguse difusiooni tõttu hõbedaosakestel), mis põhjustab fotolitograafias sekundaarse peegelduse ja harjade ekspositsiooni ning harjad lahustuvad (ilmutamisel) söövitusalustites.