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Silver nano-structures prepared by oriented evaporation on laser-patterned poly(methyl methacrylate)

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Abstract Preparation of ordered arrays of silver nano-structures with defined shape and symmetry on patterned polymer surface is described. Laser irradiation of porphyrine-doped poly(methyl methacrylate) leads to a material flow driven by temperature gradient and to creation of regular surface pattern. Subsequent shadow silver evaporation results in selective silver deposition and creation of ordered system of silver arcs. Structures produced in this way are examined using AFM, SEM, XPS, and FIB–SEM methods.

Introduction

Recent developments in photonics and optoelectronics have required design of new materials (meta-materials) with non-trivial electrical and optical properties, which are not met in nature [1]. This material combines non-trivial properties due to specific phenomena related to size and ordering effects at micro and nano-scale. Materials based on ordered array of metal nano-structures with defined size and shape are of interest in various fields. Periodical metal structures deposited onto polymer substrate can found application in plasmonics [2, 3], new photonics meta-materials [4], sensing [5], and catalysts [6]. As example, colossal increase in the Raman scattering cross-section of molecules deposited on nano-structured metal surface with defined shape reported in the work [7] can be given. Fluorescence enhancement is another perspective application of patterned metal surface [8]. Light interaction with specially designed metallic structures results in effects unattainable with naturally occurring materials, e.g., negative permeability [9], negative refractive index [10], and nonlinear effects in magnetic meta-materials [11].

Several procedures for fabricating micro-engineered metal/polymer structures have been described [12]. Some of the proposed methods are based on metal coating of polymer films with subsequent patterning by laser [13], mechanical [12], or thermal treatment [14]. Other techniques use selective metal deposition on patterned polymer surface. In this case, a structure with micro- or nano-meter scale has to be prepared on polymer surface first. There are several ways how it can be done, e.g., by electron or ion beam lithography, phase separation or laser treatment. External electrical field or temperature gradient can also be applied for polymer patterning [15–17]. At the next stage, patterned polymer surface has to be selectively coated by metal. Sputtering under well-defined conditions [18] or removal of a part of copolymer combined with special deposition procedure like electro-chemistry [19] can also lead to selective metal coating. Some of the proposed methods, like nano-particle solution processing [20], lead to 1D structure in the form of nano-wire.

In this work, a new method of preparation of 2D metal structures with arc geometry is reported. At the first stage, the PMMA films are modified by scanning with laser light combined with mechanical movement of the samples. Then the modified PMMA surface is coated with silver, and ordered array of silver strips is created. Prepared structures can exhibit "untrivial" properties due to arc shape of the silver periodical structures.

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Experimental

Materials

Poly(methyl methacrylate) (PMMA) of optical purity was supplied by Goodfellow, UK; meso-tetraphenyl porphyrine of 99.7 % grade was purchased from Frontier Scientific and 99.99 % pure silver target was obtained from Safina, CZ. All materials have been used without additional purification.

Sample preparation

Sample preparation was performed in several steps. First, the 5-μm thick layers of PMMA doped by 3.7 % porphyrine have been prepared. The polymer and dye were dissolved in dichlorethane and spin-coated onto glass substrate under 3,000 rpm. After deposition, the films have been dried for 24 h under ambient conditions [21].

In the next step, the surfaces of prepared PMMA films were modified by scanning with laser light and simultaneous mechanical movement of the samples. For laser scanning confocal optical microscope, Olympus Lext was used. Simultaneous laser scanning and mechanical movement of samples resulted in formation of regular sinusoidal pattern on the polymer surface. This method of polymer surface modification, proposed earlier in our laboratory, is schematically depicted in Fig. 1 (parts A and B). Following parameters of the sample modification were chosen: 3 μm s^{-1} velocity of the sample movement, 0.1 mW laser intensity, and 50 × 50 μm^2 scanned area. For more details, the whole procedure can be found in our previous work [21].

In the next step, the patterned polymer surface was covered with silver using a high vapor deposition technique. The deposition was performed under 10^{-6} Torr pressure and with 2 A electrical current intensity. Under these conditions, 7 nm s^{-1} evaporation rate was obtained and typically 200 ± 10-nm thick silver films were prepared. Vacuum depositions have been performed in two geometries: the "standard" one, when the silver atoms come in the direction of the substrate surface normal (0° incidence angle) and the second "shadow" one with silver atoms should be coming under glancing angle of 85°

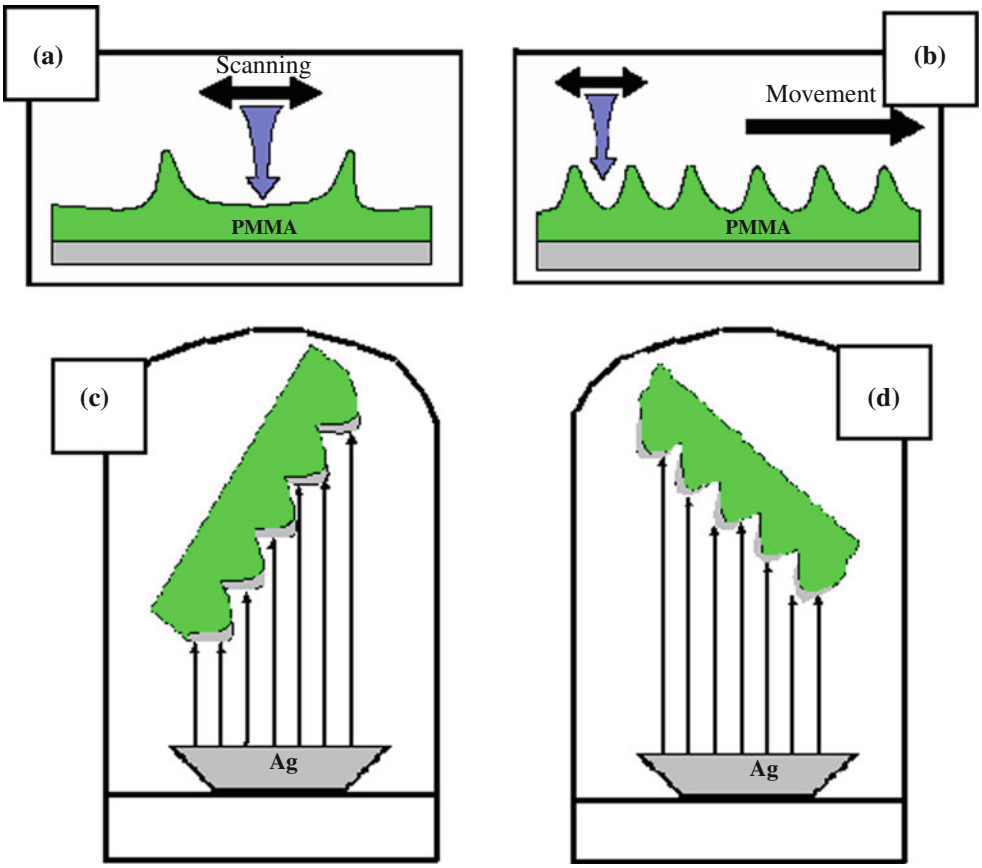

Fig. 1 Scheme of the sample preparation. **a** Surface distortion caused by laser scanning. In the next step (**b**), mechanical movement of the sample is added and the combination of both resulted in sinusoidal pattern creation. **c**, **d** Scheme of two stages of silver deposition. At dancing angle, the shadow effect leads to creation of periodical array of silver dots with arc shape

with respect to the surface normal. After the first deposition phase, the samples were rotated by 90° and deposition was performed again. The later deposition arrangement is schematically shown in Fig. 1 (parts C and D).

Diagnostic techniques

Atomic force microscopy (AFM) was used for the characterization of the sample surface. AFM measurements were performed under ambient conditions with Digital Instruments CP II set-up in tapping mode.

An Omicron Nanotechnology ESCAProbeP spectrometer was used to measure angle-resolved X-ray induced photoelectron spectra (ARXPS) [22]. The analyzed area had dimensions of 2 × 3 mm^2. The X-ray source provided 1486.7 eV monochromatic radiation. The spectra have been measured stepwise with the step in the binding energy of 0.05 eV at each of the three different sample positions with respect to the detector axis, which translated into different angles ranging from -80° to 80° (with respect to the surface normal). The spectra evaluation was carried out using CasaXPS software. The concentrations of silver, oxygen, and carbon elements are given in at.%.

Focused ion beam (FIB) cuts were prepared with an adapted scanning electron microscope (FIB–SEM, 1540 XB CrossBeam, Zeiss). After cutting with a current of 2 nA, the surfaces were polished at the lower ion current of 200 pA. The polishing procedure was performed to clean and flatten the investigated surfaces. The direct measurement of the layer thickness was done with another scanning electron microscope (JSM-7500F, JEOL). The SEM images were taken under an angle of 54°. The effect of the angle on the measured thickness was automatically corrected by the SEM software.

Result and discussion

Polymer surface modified by the laser light (measured by AFM) is shown in Fig. 2. Sinusoidal pattern can be characterized by its periodicity and amplitude [22]. The parameters can be varied in a wide range by changing experimental conditions. Concentration of porphyrine dopant and laser intensity affect the amplitude of the structure, velocity of sample movement during the laser scanning and polymer molecular weight affect mainly the pattern periodicity [21]. It is evident, that for most pronounced shadow effect in silver deposition, the ratio between pattern amplitude and periodicity must be chosen as large as possible. Present experiments were accomplished on the samples with 2.5 μm periodicity and 250 nm amplitude. (see Fig. 2).

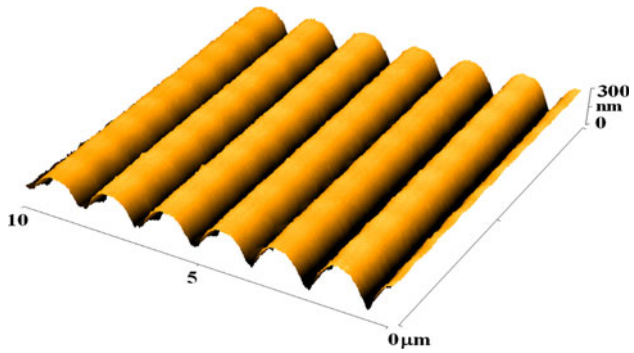

Fig. 2 AFM image of laser-modified PMMA surface doped by 3.7 % porphyrine under 3 μm s^{-1} velocity of sample movement and 0.1 mW laser power

Figure 3 shows the results of AFM imaging of laser patterned and coated with silver in standard (Fig. 3a, 0° incident angle) and shadow (Fig. 3b, 85° incident angle) deposition geometries. It is evident that depending on the incident angle, the surface profiles of the prepared structures undergo dramatic change. Periodicity and amplitude of the underlying structure are not changed, but the valleys between maxima are narrowed. Surface profiles FIB cuts in the direction perpendicular to structure ridges are shown on the bottom of parts A and B. In the case of standard coating (Fig. 3a), the cut taken on bare and silver coated polymer shows smooth and ordered profile, without any pronounced features. Quite different result is obtained for shadow deposition geometry (Fig. 3b). While the cut of bare polymer (red line) shows regular structure without any local features, the record obtained on the silver coated polymer (black line) exhibits pronounced right hand asymmetry and narrow local maxima. The most affected are tops of the structure (maxima) and the sides exposed to the silver atom beam. The surface morphology on the opposite sides, being in shadow during the deposition, is not affected. It can be concluded that in the shadow deposition geometry, the silver atoms are preferably or completely deposited on the top and one side of sinusoidally modulated structure. As was reported earlier [23, 24], the thickness of metal layer deposited on polymer surface structured by polarized laser light depends significantly on the coated site, the hill, or valley of the structure.

For the next analysis, the AFM was switched to phase mode in which the phase shift of the oscillating cantilever relative to the driving signal is measured. The phase shift reflects specific material properties (e.g., electrical conductivity, friction, or viscoelasticity) that affects the tip–sample interaction. Material properties of the samples prepared in shadow and standard deposition geometry were examined and the results are shown in Fig. 3c, d, respectively. The image of the sample prepared in standard geometry is structureless (Fig. 3c) corresponding to

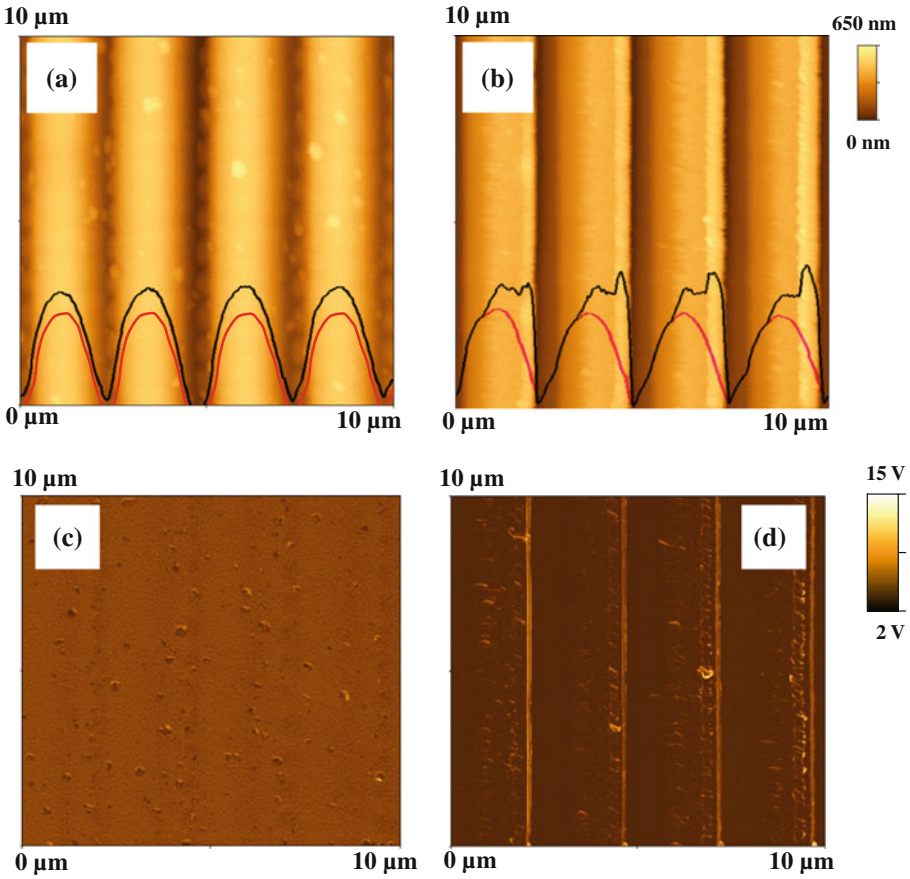

Fig. 3 **a**, **b** AFM images of modified and silver-evaporated polymer surface. The silver evaporation was performed in "standard" (0°, **a**) and shadow (80°, **b**) geometries. The *black line* at the bottom of figures gives the cut off of the structure. The *red line* shows the bare polymer profile before silver deposition. **c**, **d** the corresponding phase modes. The figure color corresponds to material properties (Color figure online)

uniform silver coverage. The sample prepared in shadow geometry (Fig. 3b) exhibits periodically varying features reflecting non-uniform silver coverage with different electrical conductivity.

Angular resolved X-ray photoelectron spectroscopy (ARXPS) is powerful technique for analysis of composition and structure of surfaces. The ARXPS measurements were accomplished in three geometries. In the first one, the measurement was performed under the angle of −80° to see the side of sinusoidal pattern uncovered with silver. In the second one, the measurement was performed in the direction of the surface normal (0°), and the third one in the measurement was performed under the angle of 80° to see opposite pattern side with silver coverage. The ARXPS results are summarized in Table 1. As could be expected, the concentration of silver increases dramatically with increasing measuring angle. Smallest silver concentration observed in the case 1 is contributed only by silver on the "top" of sinusoidal polymer pattern which can be irradiated with primary X-rays. In the second geometry, both the covered and non-covered areas of sample were irradiated by incident X-rays. Therefore, the result indicates the presence of both silver and bare polymer. As could be expected maximum silver concentration is observed in the case 3. Also, in all the measuring geometries, presence of underlying carbon and oxygen atoms is observed. In case 3, it may be due to penetration of X-ray through thin silver layer and imperfection of silver coating.

Table 1 Silver (Ag3d), carbon (C1s) and oxygen (O1s) concentrations determined from ARXPS spectra measured at different angles: (i) case 1 (−80°), (ii) case 2 (0°) and (iii) case 3 (80°)

Angle	Element concentration (in at.%)		
	C(1s)	O(1s)	Ag (3d)
Case 1 (−80°)	71.0	21.0	8.0
Case 2 (0°)	69.5	19.3	11.2
Case 3 (80°)	64.5	16.8	18.7

For details see the text

The results obtained from SEM examination of the samples are shown in Fig. 4. Samples were measured after first (Fig. 4a–c) and second stages (Fig. 4d) of Ag deposition. Image were taken before (Fig 4a, b) and after (Fig. 4c, d) ion cutting. Lower magnification image (Fig. 4a) shows clearly periodicity of the structure, but it gives no information on the structure of the silver coating. The image taken on higher magnification is shown in Fig. 4b. One can see periodically changing surface properties, the smooth regions are interrupted by grainy ones

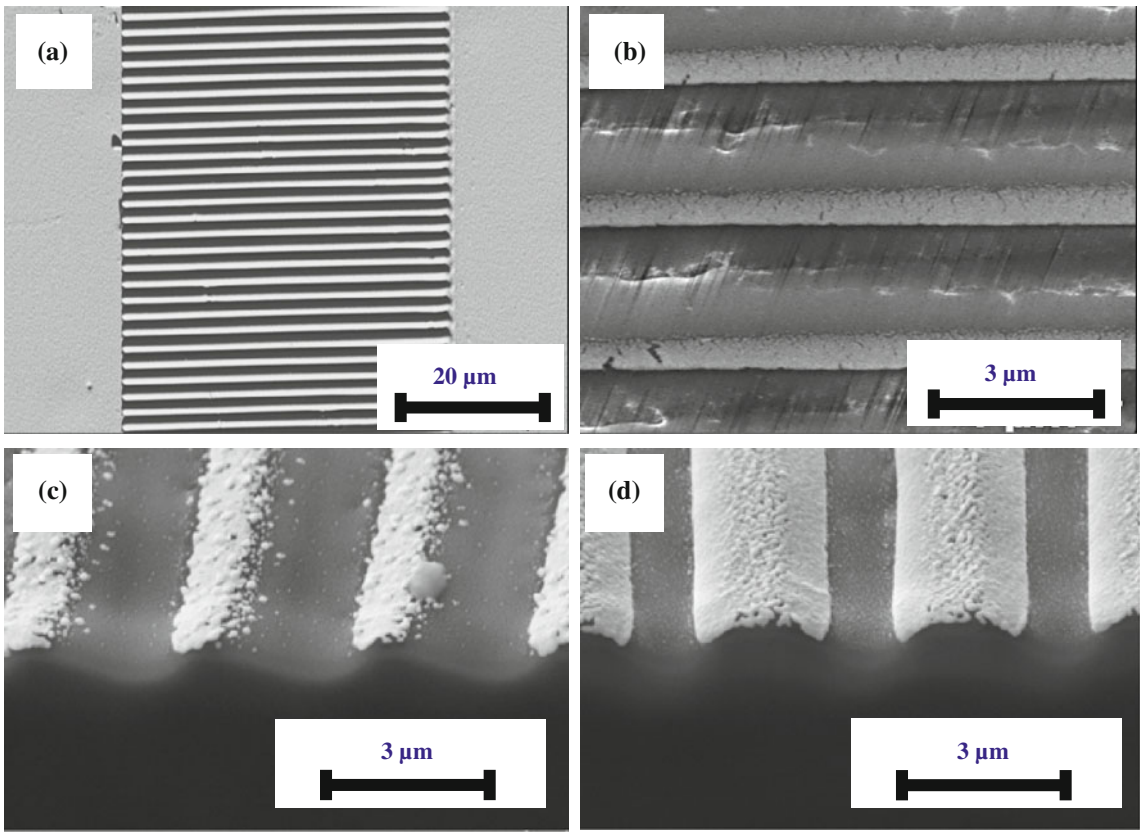

Fig. 4 **a**, **b** SEM images of structured and silver-coated PMMA taken under an angle of 90° after first stage of Ag evaporation. Some areas in the **b** indicate the sample charging (for details see the text). **c**, **d** Images from scanning electron microscope taken under an angle of 54° after cutting with current by a Ga ion beam. **c** First stage of Ag deposition and **d** the results of two stages

part A possible explanation of this phenomenon may lie in surface charging by electron beam. While silver exhibits excellent conductivity, PMMA is known as typical dielectric. When electron beam falls on sample part covered with silver, the incoming charge is well scattered because of high silver conductivity. Electron bombardment of bare polymer, on the other hand, leads to surface charging and electron beam defocusing. Smooth parts of SEM images can therefore be referred to silver-coated parts of modulated polymer and the parts with grainy structure can be referred to bare polymer.

Results of FIB–SEM measurement are shown in Fig. 4c, d. Images show the cross-section of prepared structure cut by Ga ions. The 3D location of silver is well visible from the images as lighter areas with a rough surface. Figure 4c corresponds to the first stage of Ag deposition, where the only left sides of surface maxima are covered. Appearance of the large ball in Fig. 4c can be attributed to sample defect appeared during spin-coating procedure. Figure 4d is the result of the second stage of Ag evaporation done after the sample rotation. It is evident, that prepared structures really have an accurate geometry. Silver metal arcs are well separated by polymer non-conductive areas. Prepared structures may be of interest for meta-material preparation, plasmonics, surface-enhanced Raman spectroscopy, and fluorescence enhancement. In addition, accurate structure geometry may exhibit a resonance behavior like LC resonator in a conventional electric circuit. Measurement of optical properties of the prepared structures in the infra-red wavelengths range and their possible application will be a subject of our next work.

Conclusion

Regularly ordered silver structures with accurate geometry were prepared on the surface of PMMA in two steps, the structuring of polymer substrate by laser light and depositing thin silver layer in glancing angle geometry (shadow technique) in two steps. In the first step, a sinusoidal pattern on the polymer surface is created, and in the second step, a regular system of silver arcs on the top of sinusoidal pattern is created. The prepared structures were examined using AFM, FIB–SEM, and ARXPS methods. The analysis confirms preparation of highly regular silver structure with well-defined geometry and arcs shape of silver dots.

Ordered metal structure with accurate geometry is a fundamental element of optical meta-material which could be of interest for construction of super-lens [25], or cloaking [26].

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