

Noble metals sputter deposition on water-soluble polymers

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Abstract

The nanosphere lithography is a promising and economic method easy to implement. It can be used to produce patterned nanostructures and nanoparticles arrays. This project focuses on the synthesis of Au and Ag triangle hexagonal nanoparticle arrays by nanosphere lithography and their structural characterization by atomic force microscopy (AFM). The water-soluble polymeric films can be used like a colloidal mask for metal deposition. The thin uniform polyvinyl alcohol (PVA) films were produced on the piranha cleaned and organic cleaned silicon substrates by spin-coating. The experimental dependence of the film thickness on the concentration of the solution of polymer was obtained as predicted by theory. The polystyrene (PS) nanosphere monolayer was produced on the organic cleaned silicon substrates. The Au and Ag were deposited on the PVA and PS thin films and were characterized by AFM.

Key words: nanosphere lithography, polyvinyl alcohol, polystyrene, thin films, sputter deposition, water-soluble films

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1 Introduction

Nanosphere lithography (NSL) is a powerful method, high throughput, materials general nanofabrication technique capable of producing an unexpectedly large variety of nanoparticle structures and well-ordered nanoparticle arrays [1,2].

The NSL method can be used to deposit the Au, Ag triangle hexagonal nanoparticle arrays (Fig.1) for the generation of localized surface plasmon resonance [4]. Surface plasmon resonance is the resonant oscillation of conduction electrons at the metal–dielectric or metal–air interface stimulated by incident light . The term "surface plasmon polariton resonance" explains that collective oscillation is localized within the near surface region of the nanoparticle. The useful optical properties of nanoparticles has resulted in biosensors [5], chemical sensors[6], bow-tie like infrared antennas [7], optical devices [8].

2 Theoretical Background

2.1 Nanosphere Lithography Technique

The NSL process can be divided into two steps, see Fig.2. The first step is the mask preparation. The cleaned substrate is coated with a suspension containing spherical particles (e.g., polystyrene). After drying, a close-packed monolayer of spheres, a colloidal mask, is formed. Then the material (Au, Ag, etc.) is deposited on the colloidal mask. After the deposition process the mask should be (lift-off) in ultrasonic bath in an adequate solvent.

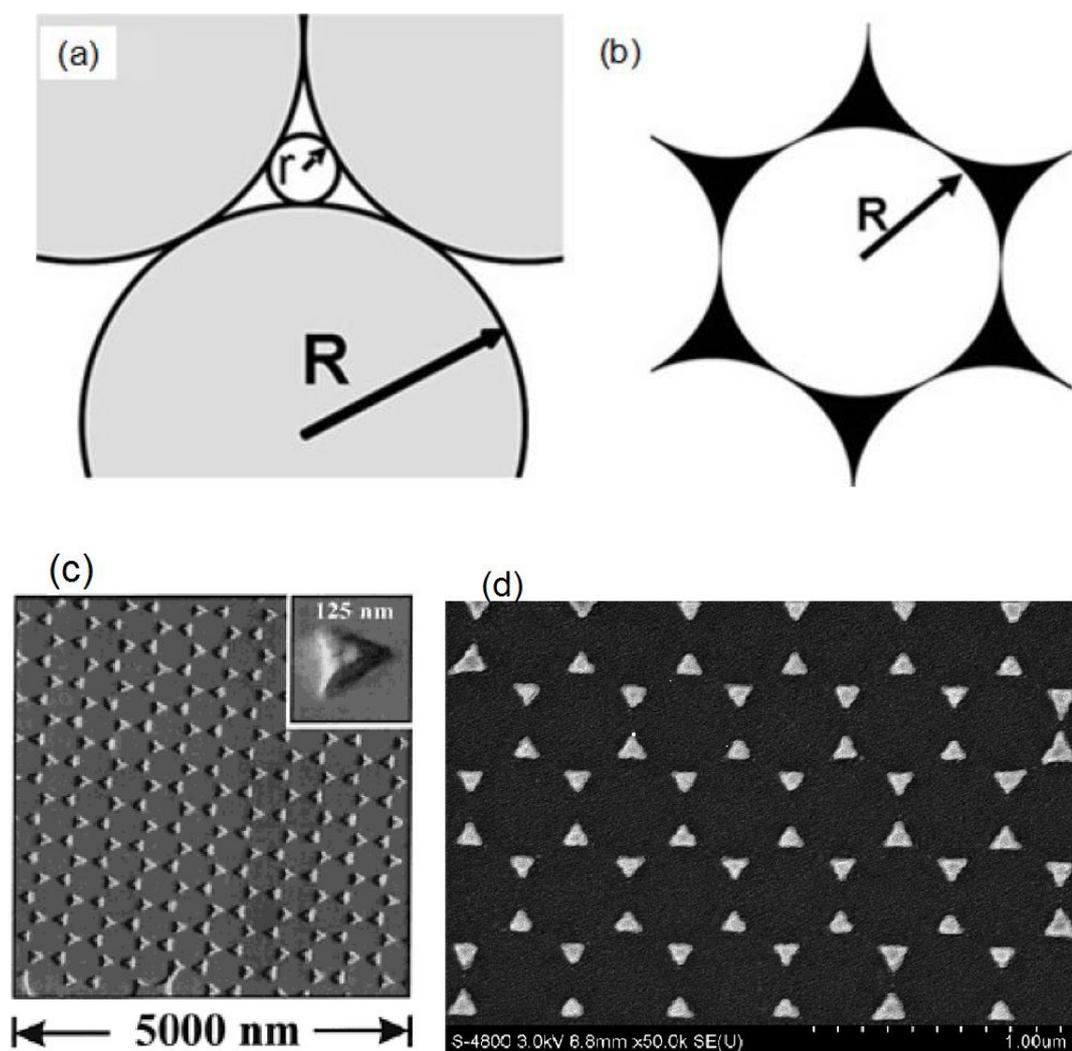


Fig. 1. (a) Hexagonal close-packed PS nanosphere structure; (b) Au-Ag triangle hexagonal nanoparticle arrays after the PS nanosphere masks were removed. [4] (c) Representative AFM image from a SL PPA fabricated with nanospheres ($D = 542$ nm) and thermally evaporated Ag metal (48 nm) [2]. (d) SEM image of topography of the triangular Ag nanoparticles fabricated by nanosphere lithography [5]

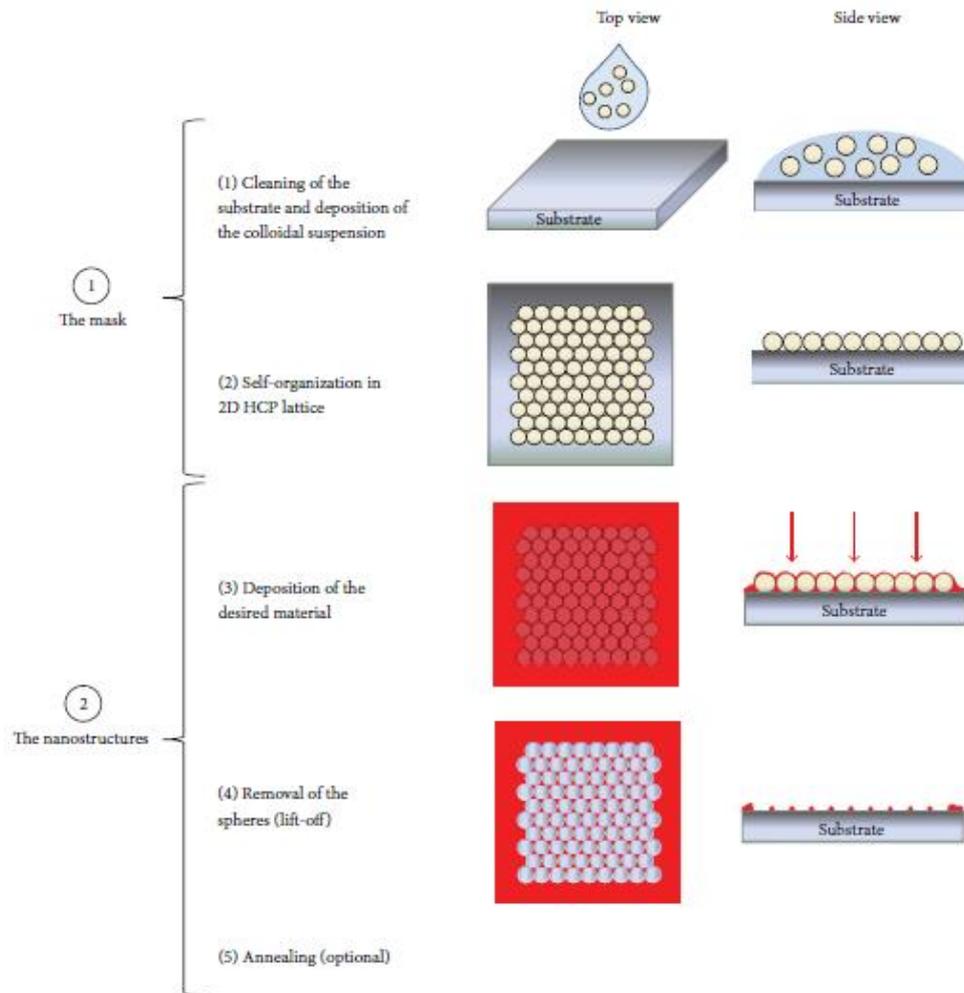


Fig. 2. Nanosphere lithography process (NSL). [3]

2.2 Water-soluble polymers

The polymer can be used as a colloidal mask. Polymer is a compound of high molecular weight derived either by the addition of many smaller molecules, as polyethylene, or by the condensation of many smaller molecules with the elimination of water, alcohol, or the like, as nylon [9]. Polymers range from natural biopolymers to synthetic plastics. The polyvinyl alcohol (PVA) or polystyrene (PS) colloids can be used as mask for nanosphere lithography process. The Polystyrene is a synthetic aromatic hydrocarbon polymer made from the monomer styrene and can be dissolved in acetone, toluene, ethanol, etc. One of water-soluble crystalline polymers is the polyvinyl alcohol or PVA. The polyvinyl alcohol is artificial nontoxic polymer, which widely used in the industrial, commercial, medical, and food sectors. This polymer can be used to produce many products, such as surgical threads, resins, lacquers, and food packaging materials, water-soluble film useful for packaging, embolization agent in medical procedures, etc. The polyvinyl alcohol can be produced via partial or full hydrolysis of polyvinyl acetate to remove the acetate groups, see Fig.3. The

structure of PVA polymer is shown in Fig.3 and hydrolysis levels vary from a typical value of 80% to reach more than 99%. The different types of PVA polymer can be produced depending on the degree of hydrolysis. The physical and chemical properties of PVA, such as the degree of crystallinity, melting point, solubility in water depend of degree of its hydrolysis and on the amount of residual ester groups. The PVA polymer is soluble in water but resistant to oils and most organic solvents. The higher the degree of hydroxylation and polymerization of the PVA, the lower the solubility in water and the more difficult it is to crystallize [10, 12]. PVA with lower degree of hydroxylation produced more soluble films (see Fig. 4), suggesting that the decrease in HD of PVA would increase its hygroscopicity and hydrophilicity [16].

The solubility in water is also affected by the molecular weight and the PVA has molecular weight in range from 10,000 to 400,000. In the Ref. [13] was shown that preferably use PVA the selected with a molecular weight in the range of from about 10,000 to about 50,000, preferably from about 20,000 to about 40,000, and more preferably from about 22,000 to 31,000. In general, at hydrolysis levels of up to 99%, polyvinyl alcohol is not water soluble, at hydrolysis levels of up to about 96-99%, polyvinyl alcohol can be dissolved in water, but the rates of dissolution are too slow to be practical, especially in cold water. At hydrolysis levels below about 85%, especially below about 79%, the polyvinyl alcohol is not sufficiently soluble [13]. But as for most polymers, for PVA the degree of solubility in water increases with increasing temperature and PVA solutions can be obtained by stirring PVA into water at 90C [12].

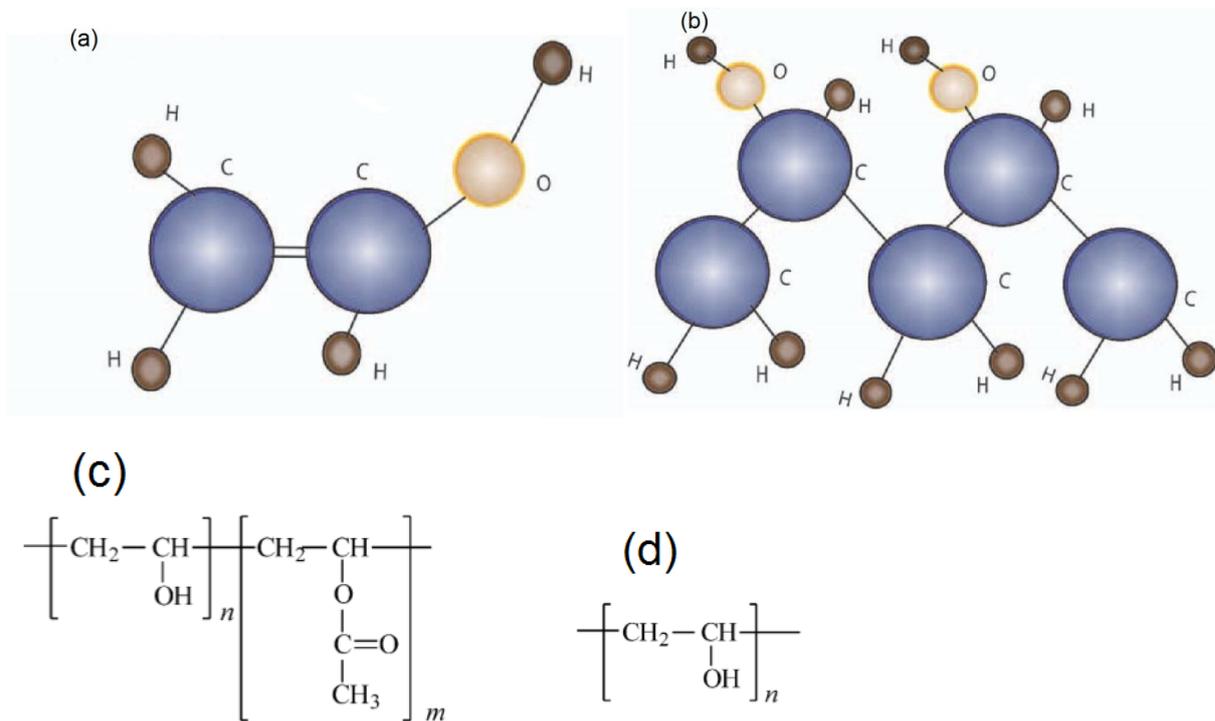


Fig 3. (a) The structure of vinyl alcohol. (b) PVA is synthesized by the hydrolysis of polyvinyl acetate [10]. Structural formula for PVA: (c) partially hydrolyzed; (d) fully hydrolyzed [11].

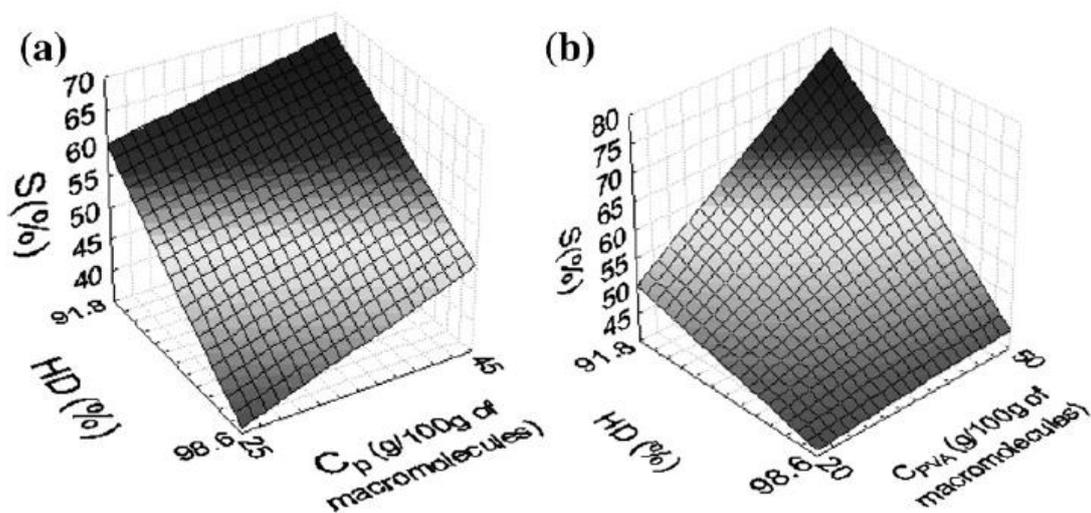


Fig. 4 Response-surfaces for solubility in water (S): (a) effect of degree of hydrolysis of PVA (DH) and plasticizer concentration (CP) and (b) effect of degree of hydrolysis (HD) and concentration of PVA [16].

2.3 Sputter deposition

The sputter deposition is a fast and thickness sensible method for the creation thin films on the top of the polymer mask. Sputtering occurs whenever any particle strikes a surface with enough energy to dislodge an atom from the surface [18]. For sputtering almost always utilizes ion bombardment, either with inert gas ions such as Ar^+ and Kr^+ , or small molecular ions such as N_2^+ , O_2^+ . During the sputter deposition the material is ejecting from a target that is a source onto a substrate such as a silicon or glass wafer. The sputtering depends on the transfer of momentum and kinetic energy from the incident particle to the surface atoms. The ions of inert gas impacts the surface of the solid target with sufficient energy to break bonds and dislodge atoms. If one or more atoms are removed from the target, they are the sputtered atoms. Then the sputtered atoms are deposited on the substrate, or deposited on the walls of the working vacuum chamber.

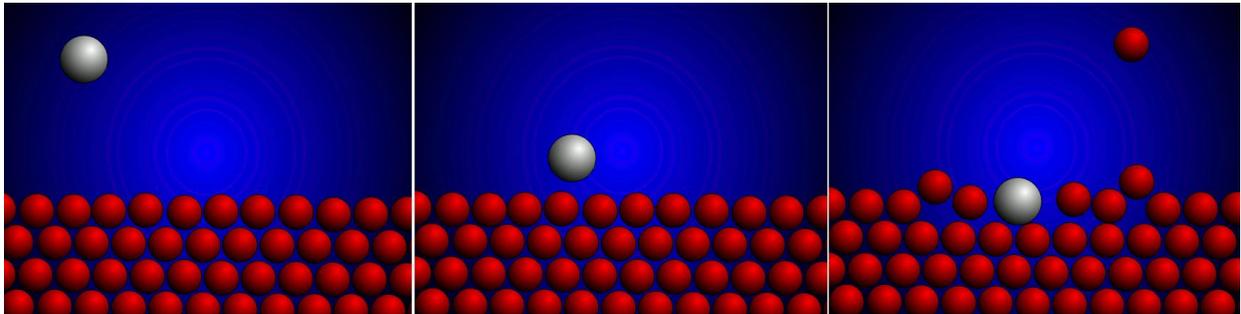


Fig. 5. The schematic illustration of the sputter deposition.

3 Experimental Section

3.1 Preparing of PVA Lithography Mask

The lithography masks were created by spin-coating PVA (average molecular weight 13,000 – 23,000 and 98% hydrolyzed) solutions with different concentration. The solutions with PVA concentration 2 mg/ml, 5 mg/ml, 7 mg/ml, 8 mg/ml, 9 mg/ml, 10 mg/ml, 12 mg/ml, 15 mg/ml were made, the de-ionized water was used. The solubility of PVA in the water depends on hydrolysis levels and rates of dissolution are too slow to dissolve PVA, especially in cold water. To dissolve the PVA in the de-ionized water was used the ultrasonic bath at a temperature of 80 °C for 2-3 hours. The thin PVA films were produced on the piranha cleaned and organic cleaned silicon substrates by spin-coating with parameters: 3000 rpm., 30 s., ramp 9, 70 μ L. The PVA crystals were dissolve in the water and homogeneous thin films were achieved, see Fig. 6.

Firstly, the piranha cleaned substrates was used for preparing thin films. The PVA polymer has strong interaction with piranha cleaned substrates. Piranha solution, also known as piranha etch used to clean organic residues off substrates and leads to hydroxylation surfaces (add OH- groups), making them highly hydrophilic. As a result, strong bonds between OH- groups of PVA (see Fig. 3) and OH- groups of the substrate were observed.

The thickness of the film was measured by scratching the sample and using the atomic-force microscope (AFM). The experimental dependence of the thin PVA film thickness on the concentration was obtained, see Fig.7.

The theoretical dependence of the film thickness on the concentration of the solution and the molecular weight of polymer was obtained in Ref. [17]:

$$d = 93.5 \text{ nm} \left(\frac{1950 \text{ min}^{-1}}{\omega} \right) \left(\frac{c}{20 \text{ g l}^{-1}} \right) \left(\frac{Mw}{100 \text{ kg mol}^{-1}} \right)^{\frac{1}{4}}$$

where d is the film thickness, $\omega = 3000 \text{ min}^{-1}$ is the spin speed, c is the PVA concentration, $Mw = 13 \text{ kg mol}^{-1}$ is the molecular weight. The film thickness is proportional to the concentration. The experimental data is in good agreement with the theory.

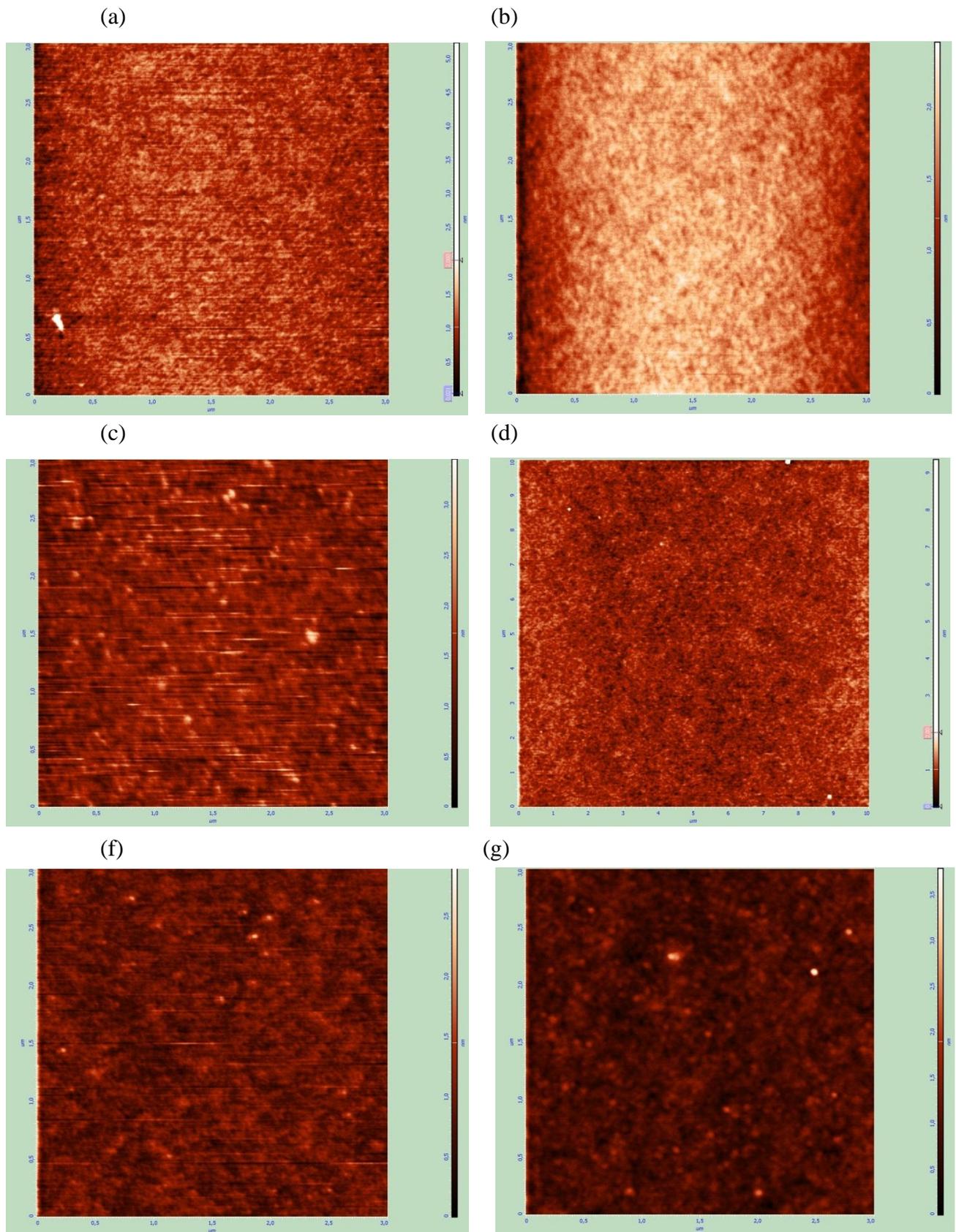


Fig. 6. The PVA thin films on the piranha cleaned substrates characterized by AFM. The different concentration of PVA solution was used: (a) 2 mg/ml, (b) 7 mg/ml, (c) 8 mg/ml, (d) 10 mg/ml, (f) 12 mg/ml, (d) 15 mg/ml.

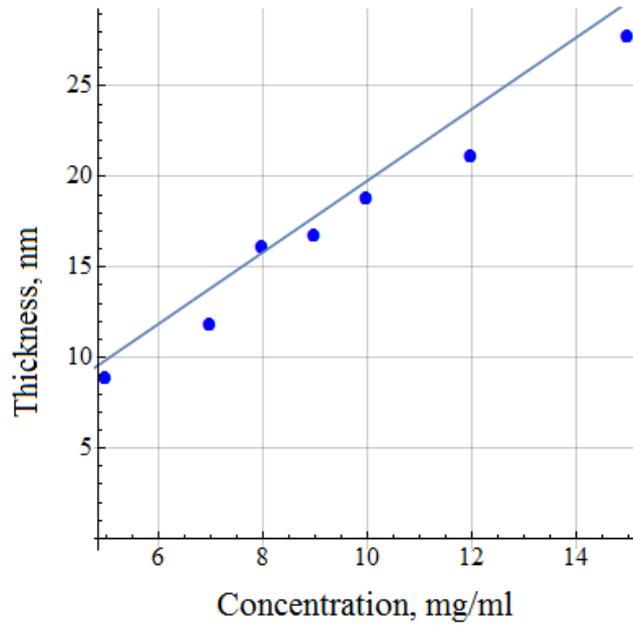


Fig. 7. Film thickness as a function of concentration. The solid line corresponds to the theory and markers correspond to the experimental data.

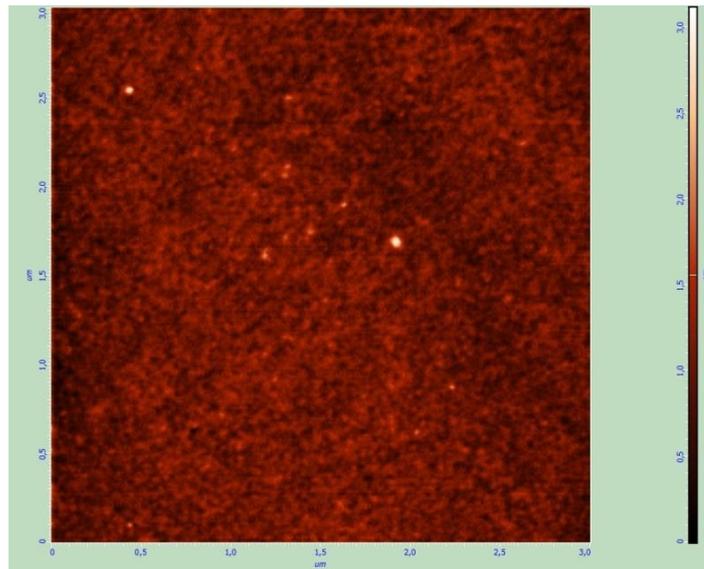


Fig. 6. The PVA thin films on the organic cleaned substrate. The 10 mg/ml concentration of the PVA solution was used. The thickness of the PVA film is 17.54 nm.

3.2 Preparing of PS Lithography Mask

For the sample preparation the Nanosphere Lithography (NSL) technique can be used. The sample preparation procedure is shown in Fig. 8.

Firstly, a clean Petri dish (10 cm in diameter) was partially filled with de-ionized water (DI) dropped along the edge using a dropper and with a dry area in the center of the dish. This dry area has three phases: water, dry glass surface of the Petri dish, and air. The drop by volume 80 μL containing 1:8 by volume ratio of PS bead solution (100 nm particles)

and ethyl alcohol was placed near the interfaces water/dry glass. The droplet of PS solution spreading on the Petri dish surface and transforms into a thin layer because it has much lower surface energy than the Petri dish glass surface. The water surface energy is higher than ethyl alcohol and due to the Marangoni effect (or Benard–Marangoni convection) [19] when the thin layer of PVA solution touches the three phase contact line (water, glass and air) convective fluid flow starts from thin PS solution layer surface to water layer surface. Due to this convective fluid flow along the surfaces, PS beads form the Polystyrene nanosphere monolayer.

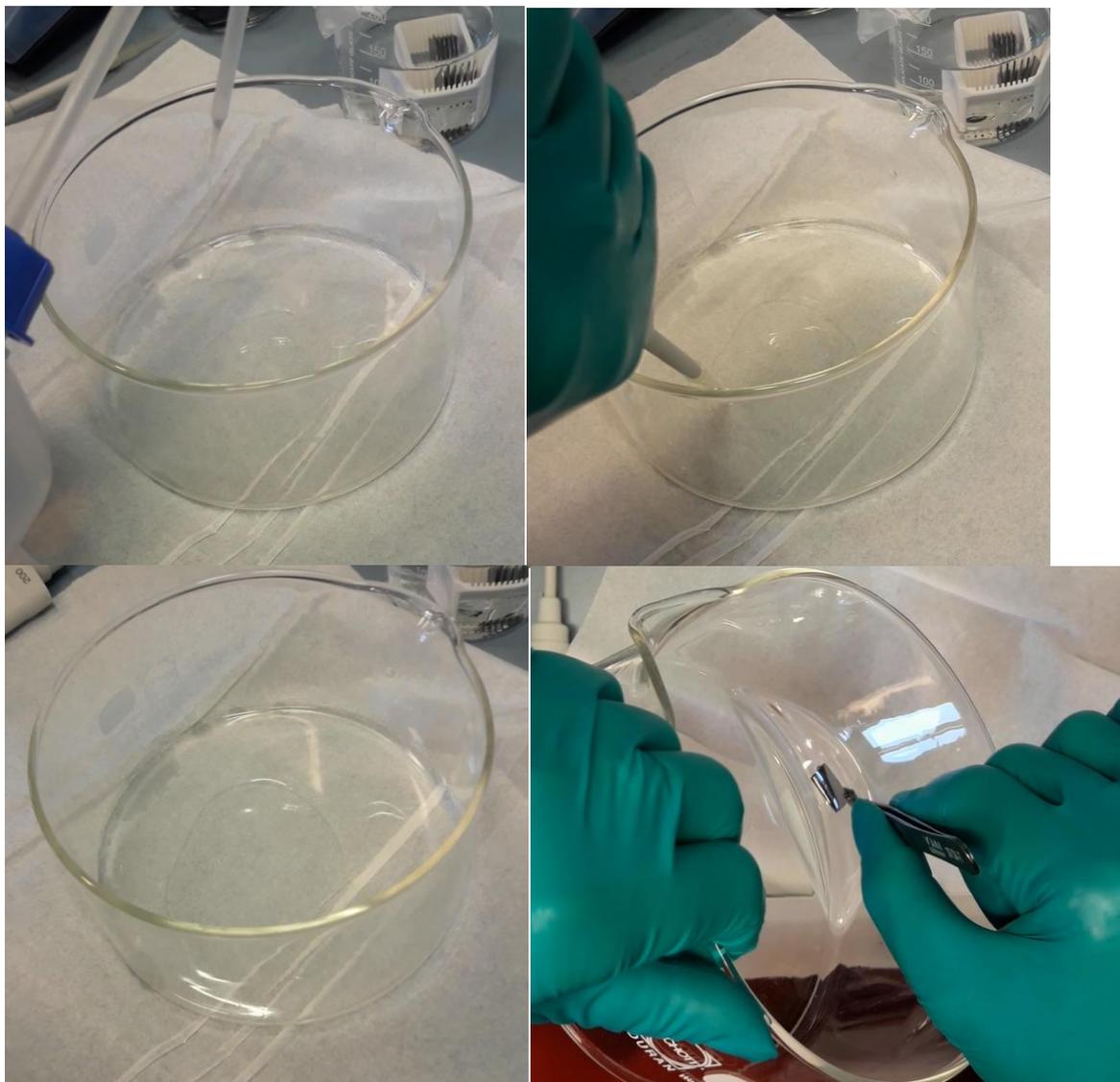


Fig. 8. Schematic illustration of the Nanosphere Lithography (NSL) technique for the preparation of the PS monolayer.

The organic cleaned Silicon substrate was vertically dipped in the DI water near the PS monolayer and were carefully removed at an angle 45° from under the PS monolayer to

transfer the monolayer onto the silicon substrate. To remove the water, the sample was heated at the temperature 50 °C. After this process the PS monolayer is formed on the substrate, see Fig.1 (a), (c),(d). The 100 nm PS colloids was used and the height of the produced films near the 100 nm, see Fig. 9 (d), so the PS monolayers were fabricated.

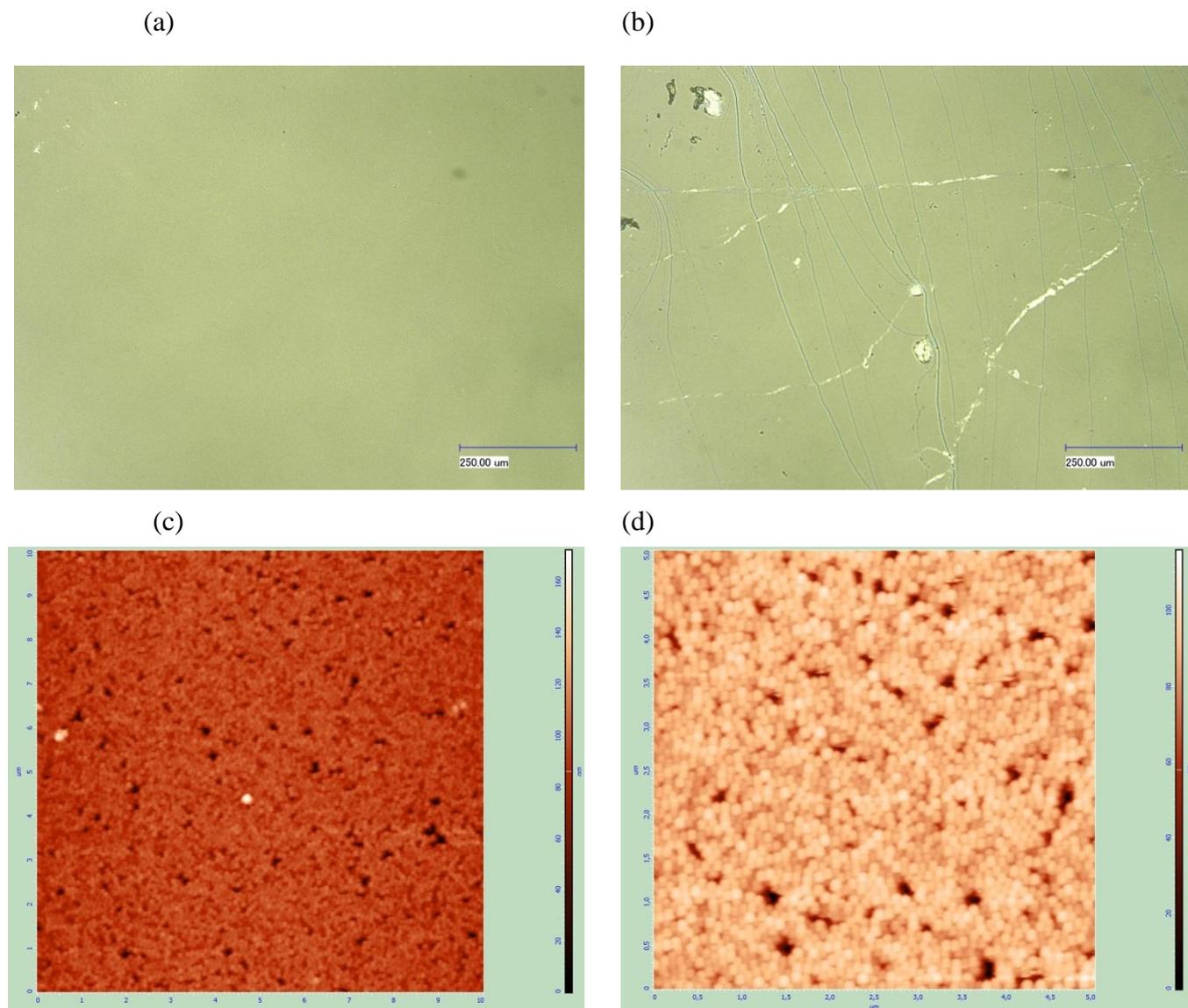


Fig. 9. The PS layers on the organic cleaned substrates. The samples was characterized by Optical Microscope: (a) the water was removed in the temperature 50 °C, (b) the temperature 90 °C was used and the stairs-like structure of PS layers was formed. The thin PS films was characterized by AFM: was measured (c) 10×10 μm and (d) 5×5 μm areas.

The described method was the most optimal, and other attempts were made. Firstly, the substrate was placed in a Petri dish, but there was not enough water volume to cover the sample completely and the close-packed PS beads layer could not be formed. Then, an attempt to vertically dip in the DI water near the PS monolayer the substrate was performed

and removed vertically, but it looked like all PS layer was flowed together with water from the substrate. Next times, the substrate was vertically dipped in the DI water and removed horizontally that so a large volume of water remained on the substrate. Also, as the water was dried at temperatures above 50 °C, the stairs-like structure of PS layers was formed, see Fig .9 (b), because the drying speed of water was too high.

3.3 Deposition of Au and Ag on the PVA thin film and PS monolayer

After the preparation of the PVA and PS lithography mask the deposition of Au and Ag was executed. The 2 nm thin films of Au and Ag were deposited on the PVA layer (10 mg/ml concentration of PVA solution was used), on the piranha cleaned and organic cleaned silicon substrates by the DF sputter deposition, see Fig. 10 and Fig. 11. The Ag clusters observed on the top of the PVA layer. The AFM measurements of the samples with deposited Au can indicate that the gold nanoparticles penetrated into the PVA layer. The PVA is a polymer that acts as a protective agent with formations in water solution and abundant OH groups; it also tends to absorb metal ions [14].

Also, 5 nm thin films of Au and Ag were deposited on the PS layer on the organic cleaned silicon substrates, see Fig. 12 .

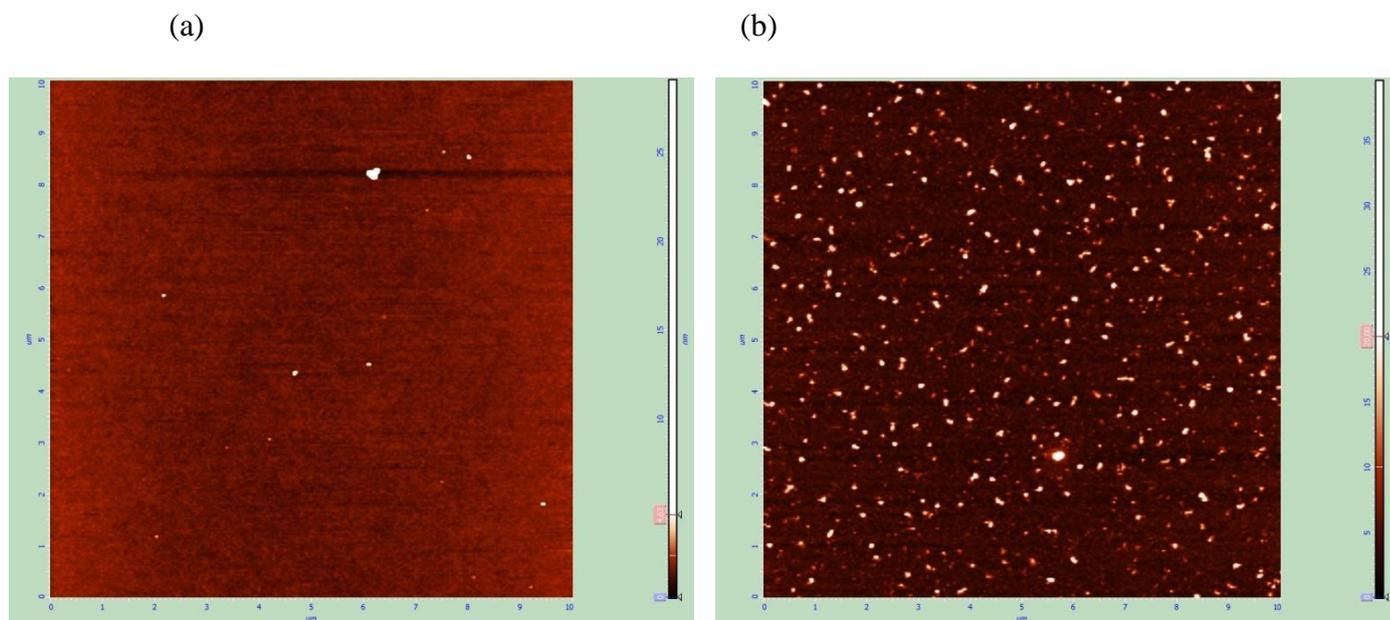
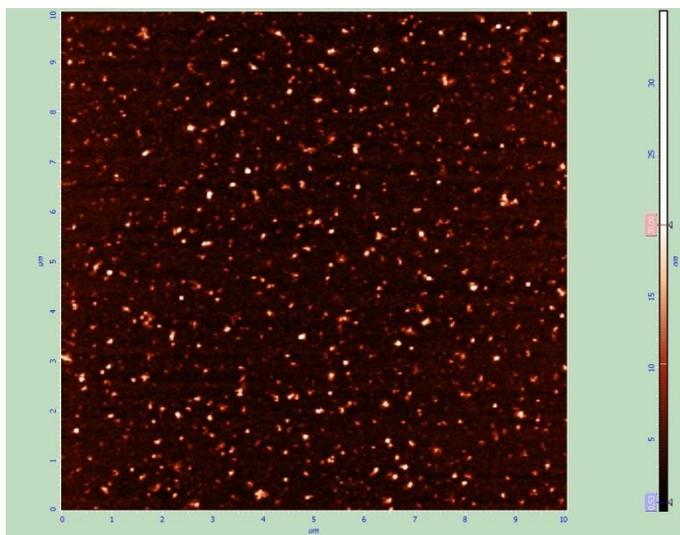
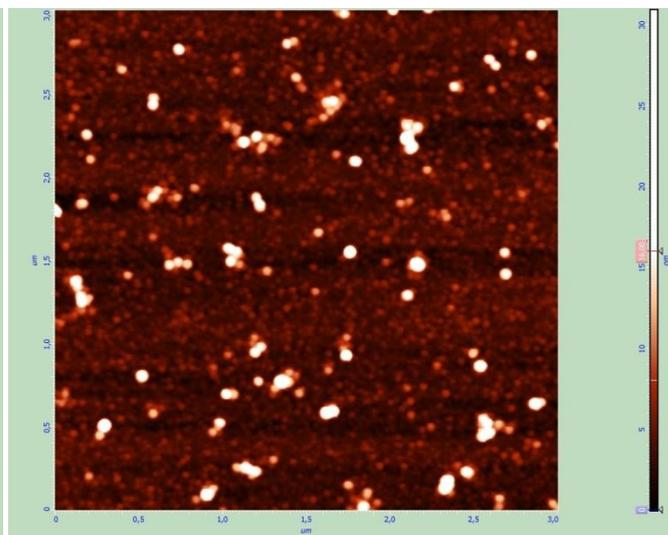


Fig. 10 The metals deposited on the PVA film on the organic cleaned substrates. The Au (a), and Ag (b) were deposited.

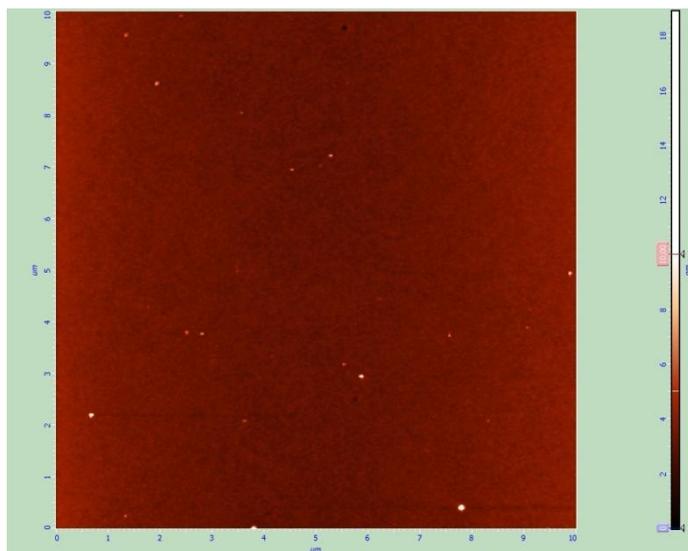
(a)



(b)



(c)



(d)

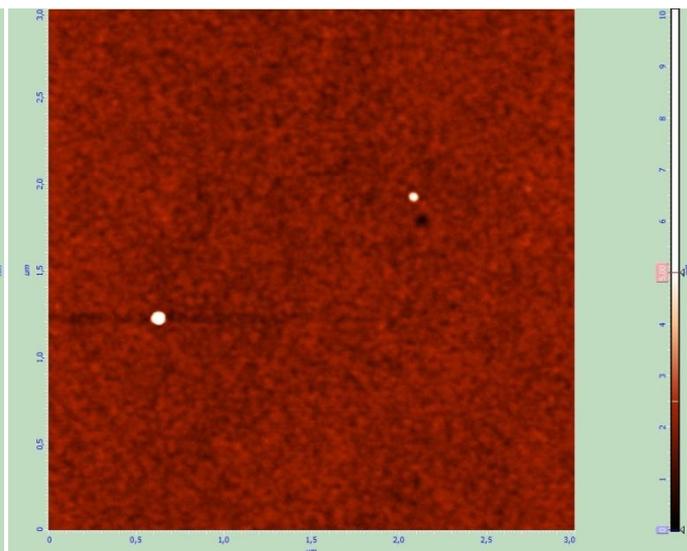


Fig. 11. The metals deposited on the PVA film on the piranha cleaned substrates. The Ag (a), (b) and Au (c), (d) were deposited.

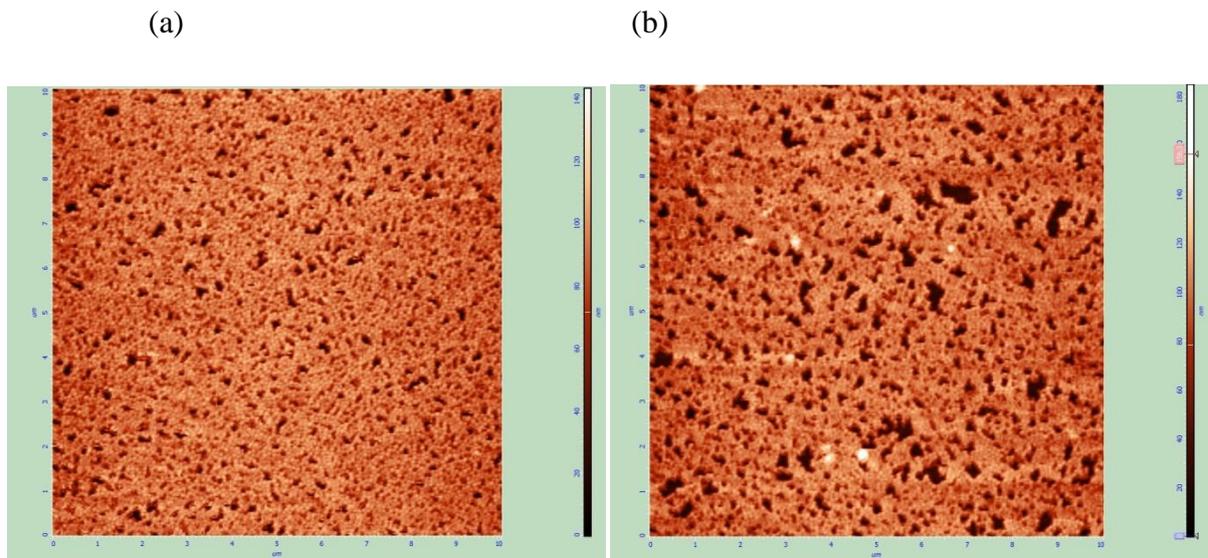


Fig. 12 The metals deposited on the PS monolayer on the organic cleaned substrates. The Au (a), and Ag (b) were deposited.

3.4 Remove the PVA mask

Solubility in the water of the PVA thin films strongly depends on type of PVA (degrees of hydrolysis and molecular weights) and it was presented in Ref. [15]. The PVA film with low degree of hydrolysis can be completely dissolved in water, regardless of molecular weights. The PVA layer can be completely removed from the organic cleaned substrates using the ultrasonic bath at a temperature of 80 °C for 2-3 hours. The upmost PVA layer can be removed from the piranha cleaned substrates due to strong bonds between OH-groups of PVA and of the substrate.

The PS monolayer can be dissolved in the acetone using the ultrasonic bath.

4 Conclusion

The solubility PVA in the water strongly depended on the hydrolysis degree. PVA with average molecular weight 13,000 – 23,000 and 98% hydrolyzed can be dissolved in the water by the ultrasonic bath at a temperature of 80 °C for 2-3 hours. The thin homogeneous PVA films was produced by spin coating on the organic cleaned and piranha cleaned substrates. All samples characterized by the AFM. Strong bonds between OH- groups of PVA and OH- groups of the piranha cleaned substrate were observed. The film thickness is proportional to the concentration of the solution. The obtained experimental dependence is in good agreement with the theory. Sputtered Ag forms unbound clusters on the surface of PVA film and the sputtered gold nanoparticles penetrated into the PVA layer.

The PS monolayer could be produced using described nanosphere lithography technique. The deposited nanoparticles penetrated into the PS monolayer.

The thickness of the deposited Au and Ag film should be optimized to achieve the triangle hexagonal nanoparticle arrays. The method to dissolve the PVA or PS films and remove the Au and Ag patterned arrays to another substrates.

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