

## Au/Ag nanostructures on PMMA surface

P.C.A. Brito, T.X.R. Souza, R.F. Gomes, N.S. Ferreira, M.A. Macêdo

*Physics Department, Federal University of Sergipe, 49100-000 São Cristóvão - SE, Brazil*

*paulabrit@gmail.com*

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Nanocavidades distribuídas densa e uniformemente em filmes de polimetilmetacrilato (PMMA) foram preparadas e analisadas, assim como o comportamento de partículas metálicas depositadas sobre a superfície dos filmes. Os filmes foram preparados pela técnica *spin-coating* e caracterizados por microscopia de força atômica. O diâmetro e profundidade médios das nanocavidades formadas na superfície dos filmes foram de 200 e 12 nm, respectivamente. Uma análise dos filmes após deposição de partículas de ouro e de prata mostra uma tendência a aglomeração dessas partículas nas bordas das nanocavidades. Verificamos que os filmes obtidos podem ser usados na formação de nanoestruturas em um processo de alto-montagem.

Palavras-chave: molde, alto-montagem, nanoestruturas.

Densely and uniformly distributed nanoholes in poly(methyl methacrylate) (PMMA) films have been manufactured and analyzed, as was the behavior of metallic particles deposited onto the films. The films had been prepared by spin-coating and characterized by atomic force microscopy. The measured diameter and depth of the nanoholes formed on the films had presented values around 200 nm and 12 nm, respectively. An analysis of the organization of both silver and gold film-deposited nanoparticles showed a tendency to agglomerate on the nanohole edges on the polymeric film surface. We verified that the films are favorable for use as templates in a self-assembly processes.

Keywords: Template, self-assembly, nanostructures.

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### 1. INTRODUCTION

The investigation and obtainment of nanostructured systems currently are areas of great scientific and technological interest because there are technical applications of this technology in many different fields, such as materials science, biomedical science, electronics, optics, magnetism and electrochemistry [1-8]. Today, there is a large variety of techniques capable of creating nanostructures to several degrees of quality, speed and cost, such as soft lithography [2,9], scratching lithography [3,9] and self-assembly [4-11]. The use of polymers in the development of templates for self-assembly of particles is extensively explored in the literature [2,4,6], and the knowledge of the physical interactions between deposited particles and polymer molecules is important for the understanding of the nanostructures formation.

Poly(methyl methacrylate) (PMMA) is classified as a hard, rigid and brittle material that has tensile, compressive and textural strengths satisfactory for many applications [12]. The films are characterized by a high light transparency (90–99%) [7]. A very common solvent for the PMMA in the preparation of films is chloroform because it has a solubility parameter ( $19.03 \text{ J}^{1/2}\text{cm}^{-3/2}$ ), which is very close to that of PMMA ( $19.00 \text{ J}^{1/2}\text{cm}^{-3/2}$ ) [13]. The use of PMMA together with other polymers in nanostructured surfaces preparation has been widely researched [5,11]. Due to differences in the surface-free energy between polymeric films and metal particles, the formation of structures is favored.

The energy of some polymers is around  $10^{-3} \text{ J/m}^2$ , while the noble metals have an energy around  $2 \text{ J/m}^2$ ; i.e., the energy of the polymer is much smaller than the energy of metal particles, which favors the formation of islands in accordance with the mode of growth Volmer-Weber [14]. To our knowledge, the use of nanostructured films using PMMA as the template for metal nanostructures has not been investigated. In this work, densely and uniformly distributed nanoholes on the surface of PMMA and their use as templates for metallic nanostructures were produced and analyzed.

## 2. EXPERIMENTAL

The solution of PMMA was obtained by dissolving 0.04 g of PMMA in 10 ml of chloroform ( $\text{CHCl}_3$ ), and the resulting solution was transparent. The experiments were carried out in the open air with an atmospheric humidity around 80%. The films had been prepared by spin-coating with approximately 0.4 ml of the PMMA solution dripped on the glass substrate. A rotation speed of 3500 rpm was used for a time of 10 s. On the PMMA film, the metallic layer of silver or of gold, with 5 nm thicknesses (estimate using quartz balance), were deposited by sputtering.

The AFM images were taken using Topometrix Acurrex-II microscope in the ambient conditions. The morphology of the surface of samples was analyzed in the intermittent contact mode, using the silicon tip mounted on a cantilever with a spring constant of 5 N/m and resonance frequencies of 160 kHz. The UV-Vis absorption spectra were measured at a Perkin Elmer Lambda 45 System spectrophotometer, with an interval of 300 to 700 nm.

## 3. RESULTS AND DISCUSSION

Figure 1a shows an AFM image of the film prepared at a concentration of 4 g/l of PMMA solution in chloroform spin coated at 3500 rpm. The holes formed showing an average diameter of 200 nm and depth around 12 nm, according with histogram in Figure 1b and 1c, respectively. We had observed in recent research [7] that the use of small amounts of water in the preparation of PMMA films leads to formation of pores. The formation of water droplets occurred during the evaporation of the solvent. After evaporation of these water droplets, the positions they previously occupied then became pores on the film surface [7]. As the solution used in the preparation of the films was prepared at ambient conditions, water molecules from the atmosphere were then present in solution, which explains the presence of pores on the film surface.

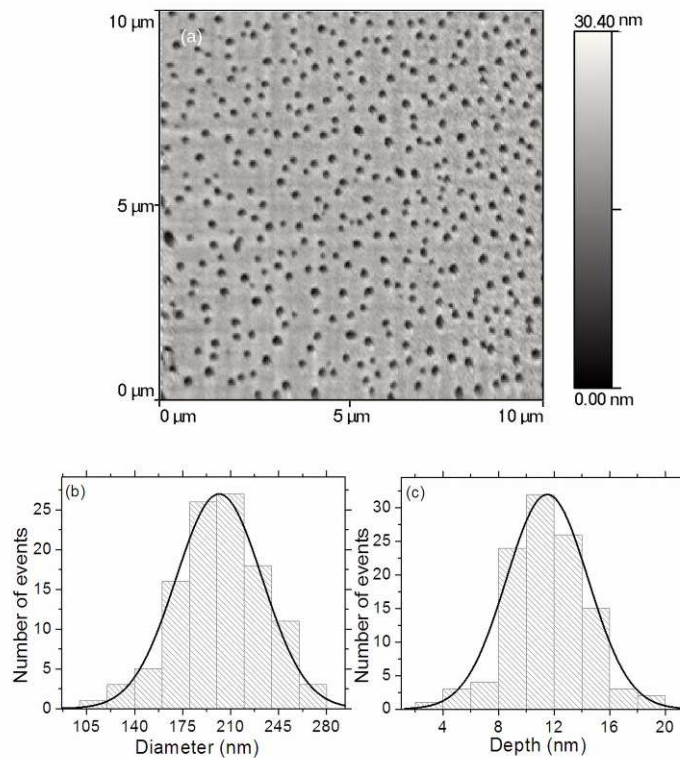


Figure 1: AFM images of samples with concentration of 4 g/l prepared with 3500 rpm. The two images to the bottom at left and at right are histograms for the variables depth and diameter, which represent the 10 x 10  $\mu\text{m}$  surface.

The film obtained was used as substrate for deposition of metal particles by sputtering (Figure 2). According to microscopy analysis, both the silver- and gold-deposited samples exhibited a tendency to form clusters on the polymer surface. Between the used thicknesses of metal deposited, the formation of nanostructures was obtained at 5 nm because thicknesses larger than 5 nm led to the holes being filled.

Figures 2a and 2b display AFM images of polymer films with Au and Ag deposition, respectively, where we observed a larger concentration of particles on the edges of the holes forming small rings on both of the films. Figures 2c and 2d show a topographic analysis of the structure formed, based on the marked line interval in the images 2a and 2b, respectively. The structure formed by the deposition of Au (Figure 2c) had an external diameter of 485 nm, thickness of 153 nm and a height of 41 nm, and the dimensions for a structure formed with the deposition of Ag (Figure 2d) had an external diameter of 735 nm, thickness of 210 nm and height of 46 nm.

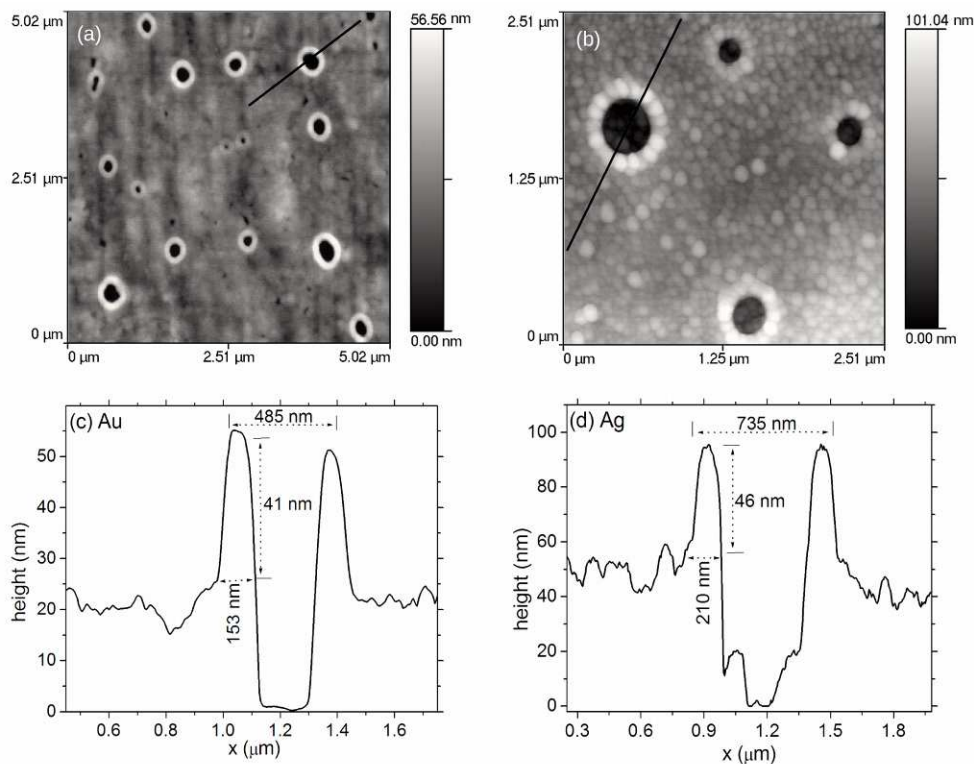


Figure 2: AFM images of samples with concentration of 4 g/l, with Au (a) and Ag (b) deposition, (c) line profile on the surface of one of the holes in the image (a) of 5x5  $\mu\text{m}$  and (d) line profile on the surface of one of the holes in the image (b) of 2,5 x 2,5  $\mu\text{m}$ .

The absorption band characteristic of both metals was observed on the polymer template as is shown in Figure 3. At graph 3a, the absorption band of Au occurs around 592 nm, which is close to the plasmon resonance of Au nanoparticles in solution with a size between 50 and 100 nm [15,16]. At graph 3b, the absorption band for the Ag was around 428 nm, which is close to the plasmon resonance of Ag nanoparticles of 25 nm in a matrix of PMMA [17] and in solution [18].

The surface-free energies of Au, Ag and PMMA are 1.6 J/m<sup>2</sup> [6], 1.3 J/m<sup>2</sup> [19], and 4.3x10<sup>-2</sup> J/m<sup>2</sup> [8], respectively. The difference in surface energies between the template and the metal implies that the atoms of metal are more strongly linked each other than they are to the substrate, causing the decrease of contact between the metal and the template surface. The metallic atoms during the deposition by sputtering became self-organized by their diffusion on the edges of the nanoholes forming small rings that minimized the system energy.

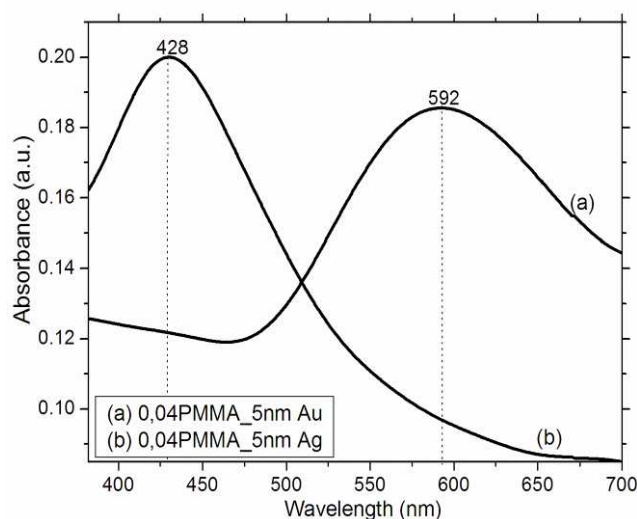


Figure 3: Room temperature optical absorbance spectra of films with 5 nm estimate thickness using quartz balance of (a) sputtered Au and (b) Ag.

#### 4. CONCLUSION

We describe the preparation of nanostructured PMMA films and the use of these films as a template for the formation of the metallic nanostructures. A uniformity of nanohole dispersion on the surface of PMMA occurred at concentration of 4 g/l of PMMA in chloroform, yielding a diameter around 200 nm and a depth around 12 nm. Due the difference in surface-free energy, metallic nanostructures were grown on the edges of nanoholes, where the contact area between metal and polymer is small. Au nanostructures were obtained with outside diameter around 400 nm, thickness of 153 nm and height of 41 nm. And Ag nanostructures were obtained with outside diameter, thickness and height around 700 nm, 210 nm and 46 nm, respectively. The plasmon resonance of the Ag and Au nanostructures were close to the plasmon resonance of the nanoparticles in solution, indicating that the PMMA films are satisfactory for use as templates.

#### 5. ACKNOWLEDGEMENT

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