SILVER COATING OF PARYLENE – C

Matei - Alexandru IONESCU[1], Robert – Cătălin CIOCOIU[2], Ion CIUCĂ[3]

Parylene-C is chemically inert and biocompatible polymer that offers a conformal and pin-hole free coating of various surfaces; it is widely used as coating for medical devices due to its excellent barrier property against body fluids. Silver coating of parylene-C should increase the anti-microbial efficiency of the parylene and cover the gap of silver and antibiotics in medical device coating. The aim of the experiments performed is to study the integrity of the Ag thin film coating of parylene-C covered medical instrumentation. The Ag coating thickness, surface morphology and mechanical characteristics translate to better protection against nosocomial infections.

Keywords: parylene-C, silver coating, nosocomial effect

1. Introduction

Health-care associated infections continue to challenge medical premises word wide [1] as more deaths have been reported than those from breast cancer and AIDS [2]. In order to qualify as an antimicrobial coating each thin film should be chemically inert, biocompatible, bio-stable, non-toxic and able to fulfill regulatory guidelines [3].

The parylene polymers have high temperature stability and low volatility making them ideal for medical instrumentation/device coating [4].

Nosocomial infections and antibiotic resistant requirements called for an increase use of silver as antibacterial agent [4, 5]. Ag is active against both Gram – negative and – positive bacteria as well as fungi [6] and it is currently used in order to prevent infections on skin burned area [7-9] or bacterial colonization of medical instrumentation or devices [8-11].

Ag as an antibacterial agent has been deposited onto various substrates: polymers, glass and titanium [12] and its use as coating for catheters has been also reported [13, 14].

Parylene-C is a class 6 FDA approved biocompatible polymer that offers a conformal and pin-hole free coating of various surfaces. Therefore, it has been

[1] Ph.D. student, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: mateiionescu@yahoo.com

[2] Assistant lecturer, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, e-mail: ciocoiurobert@gmail.com

[3] Prof., Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: ion.ciuca11@gmail.com

widely used as coating for medical devices due to its excellent barrier property against body fluids moisture and chemicals.

Antimicrobial polymers Ag coated on the inner/outer surface of the medical devices are employed as a measure to preventing its bacterial colonisation and therefore tissue colonisation on which they are attached [4].

Even though an Ag coated medical device has a risk of toxicity if the Ag nanoparticle are surpassing the concentration values given above, its efficacy in disrupting bacterial colonisation of medical instrumentation/devices cannot be questionable [15].

Endotracheal tubes, urinary catheters, vascular catheters, as well as hip prosthetics account for more than one-half of hospital acquired infections in the US [16, 17].

Methods that employ Ag as bacterial proliferation blocking agent are thin film deposition and incorporation of it into the coating that has to cover the medical instrumentation/devices [18].

Silver has a high efficiency against disease-causing microorganisms. Silver ions bind to the bacterial surface damaging it and disrupting bacterial normal function causing its death.

When silver coating a medical device, care should be taken since its toxicity is concentration dependent [15]. It has been shown that Ag nanoparticles with a concentration between $5x10^{-6}$g/ml and $10x10^{-6}$g/ml gave rise to apoptosis/necrosis in mice [15].

2. Materials and methods

Parylene C thin film was deposited via vapor deposition polymerization on Si(111) (p-Si - B as dopant – double-side polished, 5x21 mm^2, 300 μm ± 25 μm thickness, orientation <111> ± 0.5°, resistivity 0.7-1.2 Ohm-cm, MTI Corporation, Richmond, CA 94804, USA).

Parylene-C thin film grew at a rate of 0.05µm/min. (0.12mil/hour). The exact thickness measurement of the Paryelene-C thin film was done by ellipsometry and accounted for 3777nm. Thickness non-uniformity of Parylene-C thin film on Si(111) was +/- 20nm.

Ag (purity - 99.99% - Umicore, Germany) was deposited using a VU2M vacuum chamber (Russia) operated at $4x10^{-5}$mbar at 25°C. Surface sputtering lasted for t=6min. at 5Å/sec. Evaporation used a W crucible with i=180Amp/24V. Evaporation temperature was t_{evap}>961°C for a total temperature of 1200°C; density of Ag=10.5g/cm^3; resonance coefficient (z-ratio) = 0.529. Temperature monitoring was performed with an XTC controller (Inficon, Russia). The thickness of the silver thin film deposited on Parylene-C was 1997Å - *in situ* measurement, then confirmed by ellipsometry.

The samples obtained are characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM) and microhardness tests are then performed on the coated samples.

3. Results and discussion

The AFM scans were performed on 1, 9, 100 and 2500µm^2 surfaces and profile lines were traced as shown in Figs.. 1 to 4.

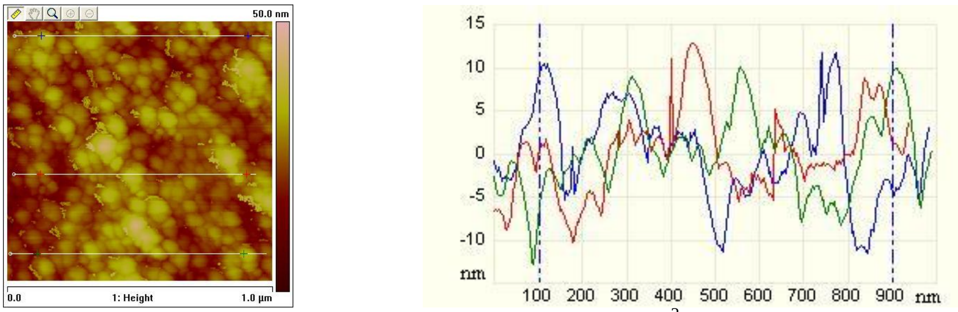

Fig.. 1 AFM image and profile lines on a 1µm^2 surface

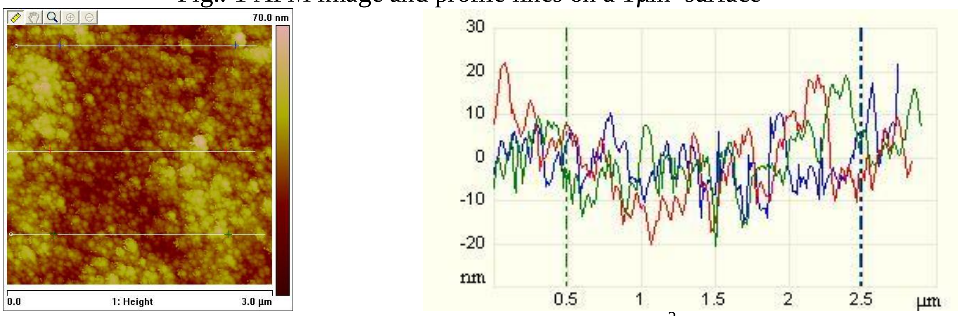

Fig. 2 AFM image and profile lines on a 9µm^2 surface

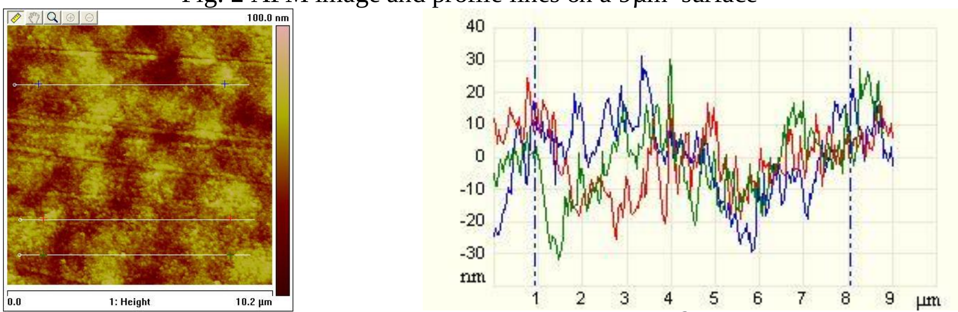

Fig. 3 AFM image and profile lines on a 100µm^2 surface

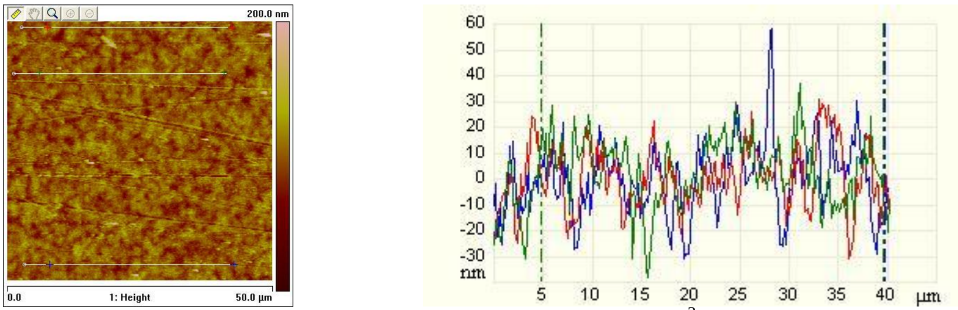

Fig. 4 AFM image and profile lines on a 2500µm^2 surface

Islands of Ag appear on the surface, as seen in Figs.. 1 and 3, which tend to merge, Figs.. 2 and 4. There appears to be a high peak to valley difference cause by the growth mechanisms of the coating: the sputtered silver shows a Volmer – Weber growth, also called an island by island growth [19] since among the silver atoms a large cohesive force exists. Increasing the sputtering time should result in island coalescence and a smoother surface.

The roughness determined on all tested surfaces is shown in table 1.

Table 1

Roughness calculated values for the investigated surfaces

Roughness/surface	2500 µm^2	100 µm^2	9 µm^2	1 µm^2
Ra [nm]	11.3	9.39	6.43	4.36
Rq [nm]	14.6	11.7	8.10	5.45

The Ra (average roughness) shows increasing values when the investigated surface was increased, similar with Rq (root mean square roughness): the average roughness is strongly dominated by shape and distribution of the islands.

In previous AFM tests performed on parylene-C the root mean square roughness obtained on a 900µm^2 the surface was 19.64nm, while on a 100µm^2 surface 16.48nm, larger than one obtained on the surface with the silver coating. The silver coating reduced the surface roughness.

The SEM micrographs obtained on the samples are shown in Figs.. 5 to 8.

The surface appears uniformly coated, as seen in Fig.. 5. The film is not defect free; holes appear as seen in Figs.. 5 and 7, but their dimensions are nanometric and should not influence the antimicrobial efficiency.

The dome shaped formations observed in Figs.. 6 and 7, so called islands, are formed during film growth. The growth mechanism of the sputtered silver film is by islands formation and coalescence, details of these stages can be clearly seen in Fig.. 8.

The Ag islands formed during coating process do not vary in size, but increasing deposition times should increase the size. The irregular shapes are signs of island coalescence. Also, a preferred orientation can be observed in Figs.. 6 and 7, which can be attributed to the parylene-C substrate.

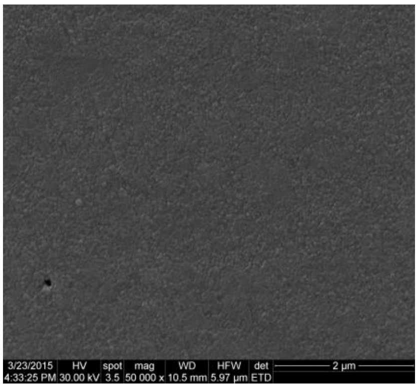

Fig. 5 SEM micrograph showing a hole on the surface

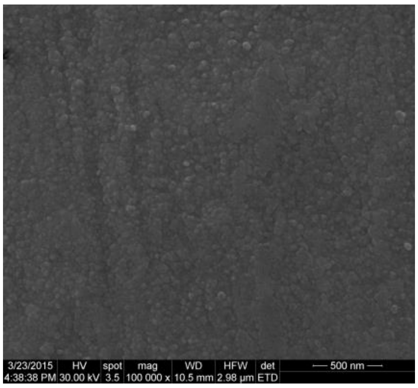

Fig. 6 SEM micrograph showing a texture which occurred during deposition

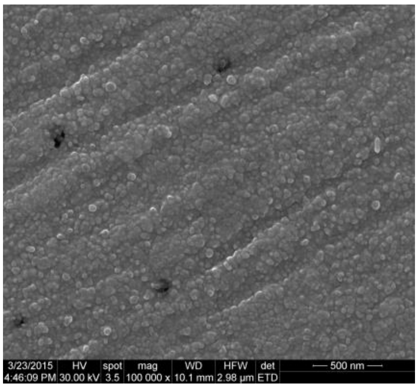

Fig. 7 SEM micrograph showing holes and a texture on the surface

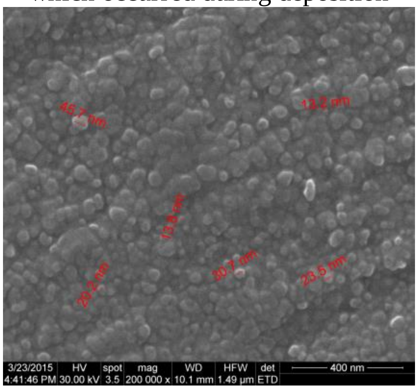

Fig. 8 SEM micrograph showing nanometric silver islands

A major role in adopting a specific growth mechanism and morphology is played, aside deposition parameters, by the substrate: the vapor deposited parylene-C showed an uneven thickness of the coating, with peaks and valleys. The silver coating had a beneficial effect in decreasing surface roughness.

The microhardness tests were performed using 5gf load. Several tests were performed/sample the mean value calculated is 27±1.57 μHV. Results from other researchers [20] regarding microhardness values for parylene C and N are shown in table 2.

Table 2

Reported values for parylene C and parylene N microhardness

Load [mN]	Vickers microhardness	
	Parylene C	Parylene N
10	296	260
20	313	283

It is obvious that, in this case, a composite hardness value is to be considered. The main contribution is to be attributed to the Ag coating which deforms and affects the result.

Fig. 9 Vickers micro-hardness imprints on the Ag coating

In Fig.. 9 the imprints show a severe plastic flow of the silver coating, while severe cracks disrupting layer integrity could not be observed. From a mechanical point of view, the silver coating does not deliver any protection: it deforms at low stresses, thus its use for mechanical active devices must be avoided.

Still, the silver coating role was to provide antibacterial efficacy: the release of Ag^+ will assure bacteriostatic and bactericidal properties.

4. Conclusion

The film morphology observed by AFM and SEM showed island like features, with signs of coalescence: the aspects revealed the island by island growth mechanism of the sputtered silver. The film was not defect free. Surface roughness was strongly influenced by island morphology and distribution; when compared with the parylene-C substrate the surface roughness decreased. Substrate morphology plays a crucial role since it dictates growth mechanism and coating morphology.

The microhardness tests and imprints revealed a strong plastic flow of the silver coating and the occurrence of small cracks. From a mechanical perspective, the silver coating does not enhance wear resistance nor has a protective role: its use in stressed medical devices must be avoided. The bacteriostatic and bactericidal properties of the coating are inherent, by releasing Ag^+ ions.

Increasing the sputtering time should modify coating morphology, decrease surface roughness and mechanical characteristics.

An increased mechanical performance of the Ag thin film could be obtained by using the sol-gel method of deposition [21].

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