Aerosol assisted plasma deposition for antibacterial coating

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Abstract: Aerosol assisted atmospheric pressure plasma deposition of antibacterial coating was developed for engineering of coatings on silicon wafer and Polyethylene terephthalate (PET) membrane. The chemical and morphological characteristics of the coatings were analyzed on silicon wafer to optimize the discharge condition. It is found that the new method is capable of composite coatings with high antibacterial deposition on both silicon wafers and PET membranes.

Keywords: aerosol assisted plasma, plasma deposition, antibacterial coating

1. Introduction

In last decades, antibacterial coatings have started to be increasingly in demand for both industrial and biomedical applications [1]. Especially in hospital, the infections from biomedical devices after surgeries bring patients into the risk of unsuccessful treatment and increased cost for period extended therapy. The initial and essential pathogenesis of infections is that microorganisms produce a polysaccharides biofilm on the surface where bacteria are exempted from the attack of antibiotics and host body's immune system, leading to the final infection. A favorable strategy to confront infection is the fabrication of proper antibacterial surfaces including micro-patterned surface, surfaces with grafted chemical groups or surface with coatings embedding antibiotics [2]. Among various antibacterial coated surfaces, coatings with silver nanoparticles (AgNPs) are regarded as a new generation of antimicrobials materials in diverse medical applications. Such kind of coatings can be engineered by means of magnetron sputtering, cluster aggregation sources, chemical methods and plasma grafting or plasma assisted deposition [3]. In recent years, aerosol assisted atmospheric pressure plasma deposition has been developed as a new method of nanometric composite coatings deposition, with the advantages of low fabrication costs, simple procedures and high versatility [4-5]. In this study, we report a novel and direct method to synthesis antibacterial coating incorporating AgNPs with aerosol assisted atmospheric pressure alternate current (AC) planar barrier dielectric barrier (DBD) plasma.

2. Experimental Setup and Methods

The experimental setup is shown in figure 1. The electrode layout was two parallel plate silver electrodes (5cm×8cm), both covered by alumina dielectric layers (0.63mm), separated by a 3 mm gap. High voltage electrode was placed on the top, while grounded electrode was located on the bottom. Both electrodes were installed in a sealed Plexiglas chamber to prevent the interference of air into discharge, as well as to insure safety protection for human respiratory system against of nanoparticles produced. The aerosols of $AgNO_3$ solution in deionized water and HMDSO were generated via pneumatic atomizers (mod. 3076, TSI)) with the use of helium gas flow. The gas flows were controlled by mass flow controllers (MSK instruments). A corona power supply was used to generate continuous mode(CM) and pulsed mode (PM, 30% duty cycle) voltage and chosen to work in high power mode (0.76 W/cm^2). Electrical parameters including voltage and current waveform were measured with a high-voltage (P6015A, Tektronix) probe and a current probe by an oscilloscope (TDS 2014C Tektronix). Prior to the deposition, pure gas flow of 4 SLM was injected for 3 minutes into the chamber to remove existing air traces. The discharge was ignited and sustained for 10 minutes in every experiment presented here. After deposition, pure helium gas flow at 4 SLM was pumped again to dispel the unused aerosols from condensing on the substrate. The substrate of Si wafer was chosen to study the influence of power mode (CM and PM) and different gas flow ratios on composition of the deposition. After optimization of the working parameters (see table 1) including power, $AgNO_3$ concentration and gas flow ratio, the substrates were replaced with PET membrane to perform the deposition of antibacterial coating for biomedical applications at different experiment conditions, shown in table 2.

Fourier Transform Infrared Spectroscopy was applied to study the functional groups of the coating with a Vertex 70V Bruker spectrometer. Scanning Electron Microscopy (SEM) was performed to investigate the samples' morphology with Zeiss Supra 40 SEM instrument. X-ray Photoelectron Spectroscopy (XPS) was carried out with a PHI-5600 Versa Probe –spectrometer to examine the atomic content of the coatings. Antibacterial assay was performed with cultures Escherichia coli (E. coli, ATCC 25922) and Staphylococcus aureus (S. aureus, ATCC 25923).

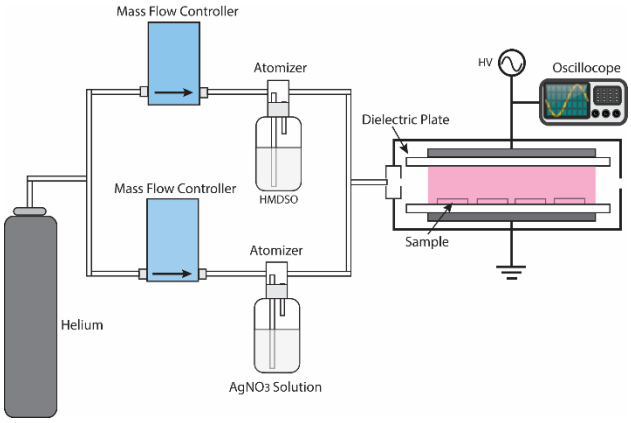

Fig. 1. Experimental setup for aerosol assisted plasma deposition of antibacterial coatings.

Table 1. Deposition conditions for engineering samples on Si wafer. Working parameters were: 10 min treatment time; 0.76 W/cm^2 power density. Samples V and W are used as the control.

Sample	HMDSO Aerosol Flow Rate	$AgNO_3$ Aerosol Flow Rate	Duty Cycle
Q	1 SLM	5 SLM	30%
S	1 SLM	5 SLM	100%
V	1 SLM	5 SLM(He)	30%
W	1 SLM	5 SLM(Water)	30%

Table 2. Aerosol flow rates used for deposition of the samples on PET membrane. Working conditions were: 10 min treatment time; 30% duty cycle; 0.76 W/cm^2 power density. Samples 4.1 and 5.1 are used as the control.

Condition	1.1	2.1	3.1	4.1	5.1
HMDSO	1 SLM	2 SLM	3 SLM	1 SLM	1 SLM
$AgNO_3$	5 SLM	4 SLM	3 SLM	5 SLM (Water)	5 SLM (He)

3. Results and discussion

The main chemical structure and the chemical bonds presented in the deposited films were examined by FTIR spectroscopy, shown in figure 2. Strong absorption bands were observed at 2965 cm^{-1} for CH_3 symmetric and asymmetric stretching vibrations, 1270 cm^{-1} for CH_3 deformation vibrations and symmetric bending in Si-CH_3 groups, 1070 cm^{-1} for Si-O-Si asymmetric stretching vibrations, 850 cm^{-1} for Si-C stretching vibrations and 800 cm^{-1} for CH_3 stretching vibrations and rocking vibrations in Si-$(CH_3)_2$ groups.

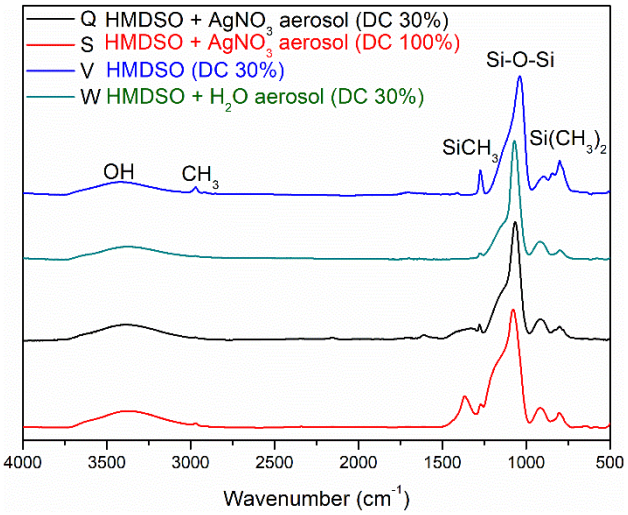

Fig. 2. FTIR spectra of samples at conditions of Q, S, V, W.

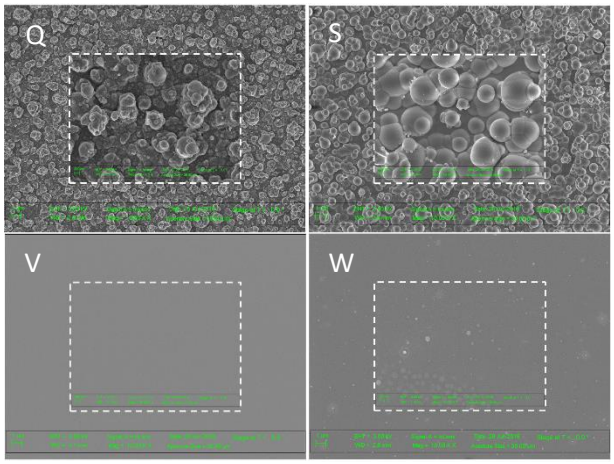

Fig. 3 SEM images of samples at conditions Q, S, V, W. Each image was obtained with 10k magnification and 50k magnification (inside the white frame).

The morphology of the coating was examined with SEM analysis, illustrated in figure 3. Figure 3(V) and (W) display the coatings without $AgNO_3$ aerosol as the control. A flat uniform coating was formed with only HMSO aerosol addition. When deionized water aerosol (0% $AgNO_3$) was injected, the coating was almost flat except some flaws caused by presence of H_2O droplets. Figure 3(Q) and (S) show the formation of nanoparticles on the substrate. Deposition at pulsed mode results in more complex structure of the nanoparticles in comparing with deposition under continuous mode.

The atomic composition of the plasma treated substrate was determined using XPS and shown in table 3. C, O, Si elements were found in all coatings. Presence of both N and Ag was observed only when $AgNO_3$ aerosol is injected in the plasma confirming incorporation of Ag and AgNO3 in the films. Higher Ag content was detected in case of pulsed mode deposition which was chosen for plasma deposition on PET membrane.

Table 3. XPS analysis of main atomic element content on the coating at conditions Q, S, V, W.

	C1s	N1s	O1s	Si2p	Ag3d
Q	46.8±2.2	0.3±0.2	35.1±1.5	13.0±0.1	5.0±0.3
S	14.4±1.6	1.3±0.5	57.4±1.0	24.3±1.2	2.5±0.6
V	6.6±0.4	0.2±0.2	64.0±0.3	28.2±0.1	0±0
W	7.7±0.8	0.7±0	63.5±0.3	28.0±1.1	0.12±0

Antibacterial activity of the treated fabrics was tested by using macro dilution method against E.Coli and S.aureus. The numbers of survived colonies of E. coli and S. aureus on the agar plates decreased for the samples with higher silver concentration. The bacterial reduction of E. coli and S. aureus is presented in figure 4 and 5. Both E. coli and S. aureus witnessed clear reduction for conditions of 1.1 and 2.1, when relatively high flow of $AgNO_3$ aerosol was delivered to the discharge zone, while no antibacterial features were observed at conditions without $AgNO_3$ aerosol.

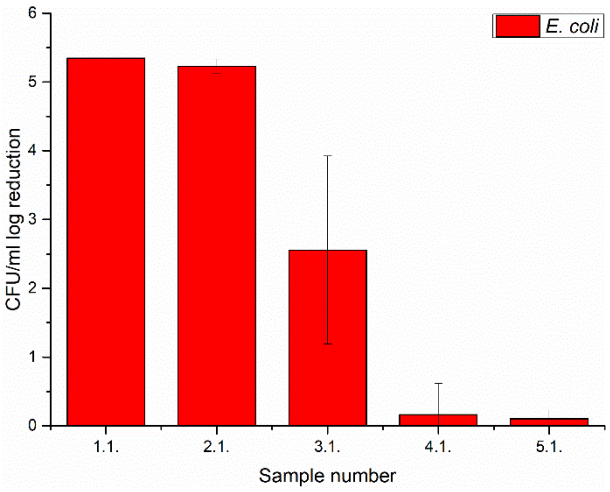

Fig. 4. Antibacterial activity of PET membrane samples 1.1 -5.1, expressed as CFU/ml log reduction for E.Coli.

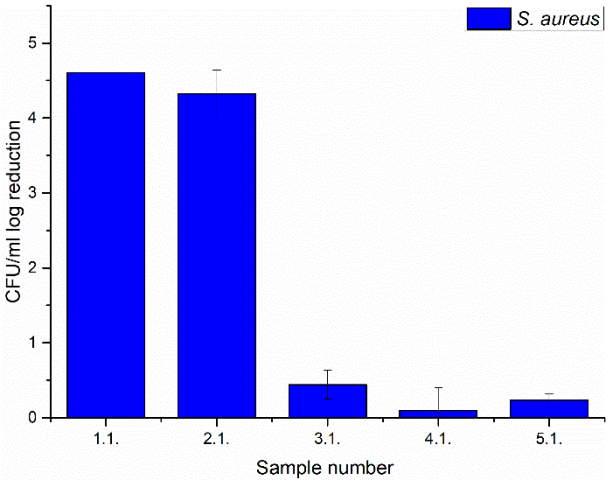

Fig. 5. Antibacterial activity of PET membrane samples 1.1 -5.1, expressed as CFU/ml log reduction for S. aureus.

4. Conclusion

Aerosol assisted synthesis of antibacterial nanocomposite was achieved in an atmospheric pressure plasma with use of AgNO3 solution. Higher Ag content was found in the pulsed mode deposition which is further selected for deposition on PET membrane. The antibacterial assay shows strong suppression of E. coli and S. aureus growth at conditions of high flow rate of $AgNO_3$ solution aerosol.

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6. References

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