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Inactivation of bacteria under visible light and in the dark by Cu films. Advantages of Cu-HIPIMS-sputtered films

A. Ehiasarian · Cesar Pulgarin · John Kiwi

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Abstract
Introduction The Cu polyester thin-sputtered layers on textile fabrics show an acceptable bacterial inactivation kinetics using sputtering methods.
Materials and methods Direct current magnetron sputtering (DCMS) for 40 s of Cu on cotton inactivated *Escherichia coli* within 30 min under visible light and within 120 min in the dark. For a longer DCMS time of 180 s, the Cu content was 0.294% *w*/*w*, but the bacterial inactivation kinetics under light was observed within 30 min, as was the case for the 40-s sputtered sample.
Results and discussion This observation suggests that Cu ionic species play a key role in the *E. coli* inactivation and these species were further identified by X-ray photoelectron spectroscopy (XPS). The 40-s sputtered samples present the highest amount of Cu sites held in exposed positions interacting on the cotton with *E. coli*. Cu DC magnetron sputtering leads to thin metallic semi-transparent gray–brown Cu coating composed by Cu nanoparticulate in the nanometer range as found by electron microscopy (EM). Cu cotton fabrics were also functionalized by bipolar asymmetric DCMSP.
Conclusion Sputtering by DCMS and DCMSP for longer times lead to darker and more compact Cu films as detected by diffuse reflectance spectroscopy and EM. Cu is deposited on the polyester in the form of Cu_2O and CuO as quantified by XPS. The redox interfacial reactions during bacterial inactivation involve changes in the Cu oxidation states and in the oxidation intermediates and were followed by XPS. High-power impulse magnetron sputtering (HIPIMS)-sputtered films show a low rugosity indicating that the texture of the Cu nanoparticulate films were smooth. The values of R_q and R_a were similar before and after the *E. coli* inactivation providing evidence for the stability of the HIPIMS-deposited Cu films. The Cu loading percentage required in the Cu films sputtered by HIPIMS to inactivate *E. coli* was about three times lower compared to DCMS films. This indicates a substantial Cu metal savings within the preparation of antibacterial films.

Keywords Cu films · Sputtered films · Polyester

1 Introduction

Cu bactericide properties have been known for decades (Page et al. 2000). The field of antibacterial Cu films/surfaces has gained much attention during the last decade since they decrease/eliminate hospital-acquired infections involving antibiotic-resistant bacteria surviving for long times (Foster et al. 2010) (Dunlop et al. 2010). The Cu films avoid chemicals to clean/disinfect hospital rooms leaving residues after use (Kramer et al. 2006). Recently, Gabbay et al. (2006), Borkow and Gabbay (2008) and also Gedanken (2004) have reported the application of Cu textiles composites as antimicrobial surfaces.

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A. Ehiasarian
Material and Engineering Research Institute Sheffield Hallam University,
Howard St,
Sheffield S11WB, UK

C. Pulgarin (✉) · J. Kiwi (✉)
Group of Electrochemical Engineering, EPFL-SB-ISIC-GGEC,
Station 6,
CH-1015 Lausanne, Switzerland
e-mail: cesar.pulgarin@epfl.ch
e-mail: john.kiwi@epfl.ch

We address the bacterial inactivation kinetics and properties of Cu nanoparticulate films sputtered by three different methods: direct current magnetron sputtering (DCMS), direct current pulsed magnetron sputtering (DCMSP), and high-power impulse magnetron sputtering (HIPIMS). Recently, our group has reported direct current magnetron sputtering by DCMS (Castro et al. 2010) and direct current magnetron pulsed sputtering by DCMSP (Osorio et al. 2011) to deposit Cu on textiles.

Wet methods to deposit Cu on fabrics produced films with low uniformity and poor adherence (Torres et al. 2010; Yuranova et al. 2006), and this moved us to use techniques depositing meta/metal ions with higher energy presenting an acceptable film uniformity (Mejía et al. 2010)

HIPIMS proceeds with a higher density of electrons/metal ion pairs and at higher energies compared to DCMS and DCMSP (Ehiasarian et al. 2008; Lin et al. 2010; Sarakinos et al. 2010) The Cu-loading necessary in the Cu films sputtered by HIPIMS to inactivate *Escherichia coli* was about three times lower compared to DCMS-sputtered films (Kusiak-Nejman et al. 2011). This indicates a substantial Cu metal savings within the preparation of antibacterial films.

This study describes using traditional sputtering methods: (a) the relation between structure and reactivity of the Cu clusters deposited by sputtering on cotton towards the inactivation of *E. coli* focusing, (b) the identification if the Cu ions on the cotton textile intervening in the *E. coli* inactivation by X-ray photoelectron spectroscopy (XPS), and (c) the increase the Cu particle density as a function of Cu-sputtering time.

Furthermore, recent work by Cu–HIPIMS describes: (a) the HIPIMS Cu deposition at two different energies (currents) and their effects on the Cu film thickness, (b) the *E. coli* inactivation kinetics as a function of the Cu-sputtering time for HIPIMS, and (c) the Cu redox states during *E. coli* inactivation along the identification of the oxidative intermediates during the bacterial inactivation process. The Cu polyester fabrics sputtered by HIPIMS were analyzed for the percentage of Cu by weight per square centimeter by X-ray fluorescence. The ionization percentage of Ar^{+}, Ar^{2+}, Cu^{+}, and Cu^{2+} are quantified by gas-phase mass spectrometry for the HIPIMS and DCMS plasma species.

2 Experimental section: materials and methods

Direct current magnetron sputtering (DCMS) loading of textiles The positive Ar ions near the target are accelerated towards the target surface by applying high negative voltages (0.2–2.0 kV). The 5 cm diameter (Lesker AG, Hastings, East Sussex, UK) Cu disk is eroded by the Ar ions and the ejected Cu atoms/clusters/ions are collected on the cotton. The plasma working pressure was in the range of 0.1–1 Pa, the distance between the Cu-target and the cotton was ~10 cm and the deposition current was 30 mA. The adhesion of Cu to the cotton (ex Cilander AG, Herisau, CH-1,109 Switzerland) was so strong, that friction with paper or cloth did not allow smearing of the Cu. This is an improvement respect to the adhesion of Cu particle fixed on activated textiles by adhesion of high surface area CuO suspensions as reported recently. Deposition times of 20, 40, 90, 180, and 360 s lead to Cu layers of 1.5, 3.0, 7.8, 16, and 28 nm thickness on the cotton surface. The film thickness was determined with a profilometer (Alphastep500, TENCOR). A stylus, loaded with 4 mg and a tip radius of 5 μm probed the film surface (Castro et al. 2010).

Direct current pulsed magnetron sputtering (DCMSP) loading of textiles Applying a current of 300 mA needed a bias voltage of −400 V. DCMSP was operated at 50 kHz with 15% reversed voltage. A negative voltage was applied of 430 V and then the voltage is switched to 65 V (15% of 430 V) leading to a power density of about 6.6 W/cm^2 to accelerate the Cu particles towards the substrate. During DCMS sputtering pulses of 10 μs were applied, but with time the target gets overcharged and when this occurs. The mode of operation is neither: (a) unipolar pulsed sputtering, where the target voltage is pulsed between the normal operating voltage and ground nor (b) bipolar pulsed sputtering where the target voltage is reversed and becomes more positive during the pulse-off period leading to bipolar asymmetric sputtering (Osorio et al. 2011).

HIPIMS sputtering on polyester, materials, and Cu film calibration HIPIMS deposition of Cu was carried out in a CMS-18 Vacuum system from Kurt Lesker Ltd. evacuated to 10^{-5} Pa by a turbomolecular pump. The Cu target was 5 cm in diameter, 99.99% pure from K. Lesker Ltd. UK. The mass spectrometry measurements were carried out in a Hiden Analytical Ltd PSM003 unit to determine the ion composition of the ions in the plasma Ar atmosphere. The HIPIMS was operated at 100 Hz with pulses of 100 μs separated by 10 ms. The HIPIMS short pulses avoid a glow-to-arc transition during plasma particle deposition. The polyester used corresponds to the EMPA test cloth sample no. 407. It is a polyester Dacron, type 54 spun, plain weave ISO 105-F04 used for color fastness determinations. The values of the thicknesses of the Cu films for diverse sputtering times using HIPIMS is shown in Table 1. For 21-s deposition time with 6 amps a thickness of 28 nm was found. A deposition time of 61 s at 60 amps led to a 28 nm Cu layer.

X-ray fluorescence determination of Cu nanoparticulate film (XRD) The Cu content of the most relevant samples of polyester/Cu deposited by HIPIMS was evaluated by X-

Table 1 Sputtering time and thickness for Cu-layers by HIPIMS at 6 and 60 amps

	Deposition time [s]	Power [amps]	Thickness [nm]	Cu [% wt]
HIPIMS	2	6	1.5	0.0121
	4	6	4	0.0200
	18	6	16	0.0600
	21	6	28	0.1120
	3	60	1.5	0.0073
	7	60	3	0.0182
	35	60	16	0.0675
	61	60	28	0.1020

ray fluorescence. The spectrometer used was RFX, PANalytical PW2400.For the two most effective loadings of Cu on polyester a deposition time of 21 s with 6 amps led to 0.112 wt.% Cu/wt polyester and a deposition time of 61 s at 60 amps led to 0.102 wt.% Cu/wt polyester.

Bacterial inactivation evaluation of E. coli on Cu nanoparticulate film The samples of *E. coli* (*E. coli* K12) was obtained from the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ) ATCC23716, Braunschweig, Germany to test the antibacterial activity of the Cu textiles. The textiles was sterilized by autoclaving at 121°C for 2 h. Twenty microliters aliquot of culture with an initial concentration of 3.8×10^8 CFU mL^{-1} in NaCl/KCl was placed on each coated and uncoated (control) fabric. The samples were placed on Petri dish provided with a lid to prevent evaporation. After each determination, the fabric was transferred into a sterile 2-mL Eppendorf tube containing 1 mL autoclaved NaCl/KCl saline solution. This solution was subsequently mixed thoroughly using a Vortex for 3 min. Serial dilutions were made in NaCl/KCl solution. A 100-μl sample of each dilution was pipetted onto a nutrient agar plate and then spread over the surface of the plate using standard plate method. Agar plates were incubated, lid down, at 37°C for 24 h before colonies were counted. The experiments reported were replicated at three times (Castro et al. 2010).

Electron microscopy of Cu nanoparticulate films (TEM) A Philips CM-12 (field emission gun, 300 kV, 0.17 nm resolution) microscope at 120 kV was used to measure the particles size of the Cu nanoparticles. The textiles were embedded in epoxy resin 45,359 Fluka and the fabrics were cross-sectioned with an ultramicrotome (Ultracut E) and at a knife angle at 35°. Images were taken in Bright Field.

X-Ray photoelectron spectroscopy of Cu textiles The X-ray photoelectron spectroscopy of polyester/Cu samples (XPS) used an AXIS NOVA photoelectron spectrometer (Kratos Analytical, Manchester, UK) equipped with monochromatic AlKa (hν=1,486.6 eV) anode was used. The carbon C1s line with position at 284.6 eV was used as a reference to correct the charging effect. The quantitative surface atomic concentration of some elements was determined from peak areas using sensitivity factors (Wagner et al. 1979). Spectrum background was subtracted/corrected for electrostatic charging according to Shirley (1975).

3 Results and discussions

DC-magnetron sputtered semi-transparent Cu gray–brown films (Castro et al. 2010) on cotton are effective in the inactivation of *E. coli K12*. Figure 1 shows the inactivation of *E. coli* on Cu-sputtered samples by DC pulsed magnetron sputtering (DCMS). Cotton by itself did not inactivate the *E. coli*. The 40-s Cu-sputtered samples lead to full bacterial inactivation within 120 min in the dark and 30 min irradiated under low intensity visible light having ~1% of the full solar light irradiation (AM1). The 180-s Cu cotton-sputtered samples lead to a complete bacterial inactivation within 30 min under light and 120 min in the dark of having a Cu content of 0.294% Cu wt./wt. cotton or five times above the Cu-deposited with 40 s sputtering inactivating completely *E. coli* within the same time. A sputtering time of 40 s leads to the most favorable structure–reactivity for the Cu clusters inducing the shortest *E. coli* inactivation.

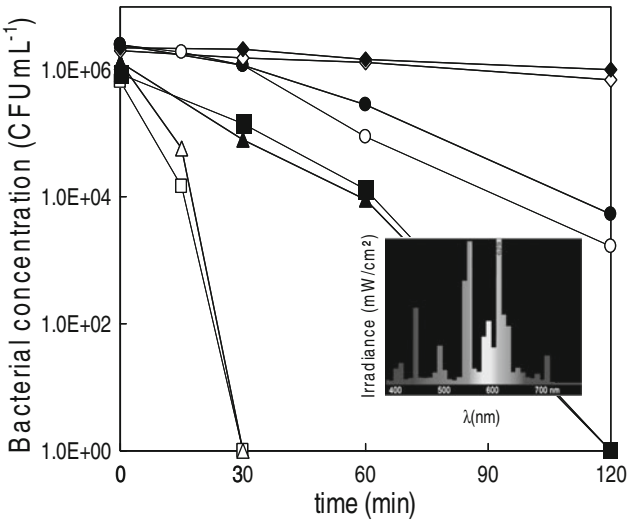

Fig. 1 *E. coli* inactivation for cotton: light (*diamond operator*), dark (*black diamond*), and Cu DC magnetron-sputtered cotton samples at times: 20 s dark (*black circle*), light (*white circle*); 40 s dark (*black square*), light (*white square*); 180 s dark (*black triangle*), light (*white triangle*).The spectral distribution of the visible light source used of 1.2 mW/cm^2 is shown in the *insert*

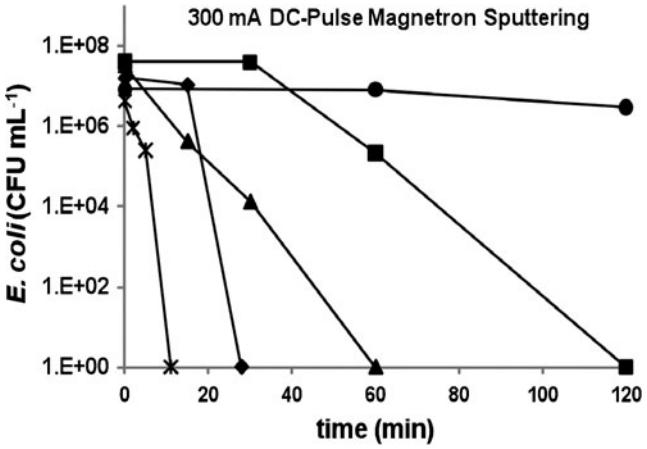

Fig. 2 *E. coli* inactivation by Cu cotton in the dark: Cotton alone (*black circle*); 4 s (*black square*); 20 s (*black triangle*); 40 s (*black diamond*); 60 s (*Latin small letter x*)

Figure 2 presents the *E. coli* inactivation by Cu samples prepared by DCMS magnetron sputtering (Osorio et al. 2011). In this case, dark runs led to 30 min *E. coli* inactivation which is a much shorter time compared to the inactivation time needed by DCMS under the same conditions as shown in Fig. 1.

Applying 300 mA DCMSP for 4 s lead to the threshold loading of Cu for *E. coli* inactivation on a sample 0.048% wt. Cu/wt. cotton. The fastest *E. coli* inactivation within 10 min in Fig. 2 was carried out with a Cu sample sputtered for 60 s with a 0.269% wt. Cu/wt. cotton with a loading of 10^{16} atoms/Cu/cm^2 or a coating thickness of 1.0–1.2 nm (five to six Cu layers). The higher energies of the Cu ions used in the DCMSP up to 100 eV deposit Cu nanoparticles with a different structure/properties than the ones deposited by DCMS at energies of 5–15 eV (Lin et al. 2010). The significantly higher bacterial inactivation activity of the Cu fixed on cotton by DCMSP suggests that Cu sites exposed on the surface or inside the cotton interact with *E. coli* regardless of any agglomeration on the surface of the cotton fiber. This is different to the cotton with DCMS samples

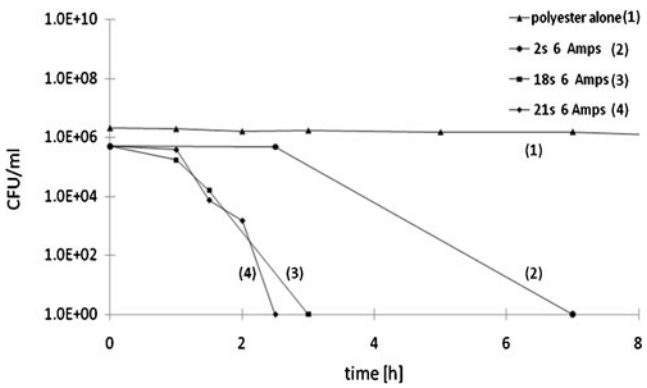

Fig. 3 Kinetics of the *E. coli* inactivation in the dark by HIPIMS Cu-deposited samples using 6 amps

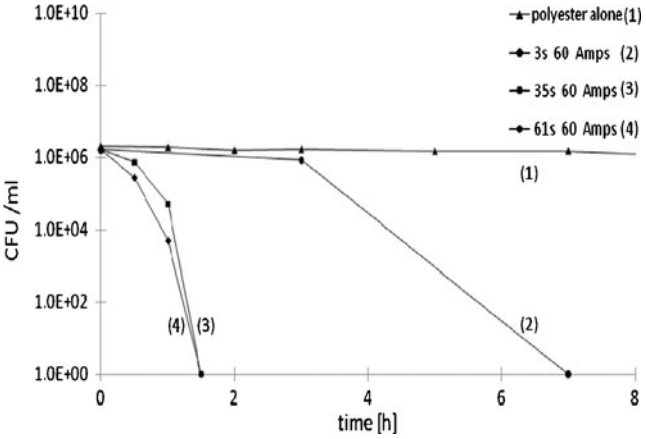

Fig. 4 Inactivation kinetics of *E. coli* on Cu HIPIMS polyester films sputtered with 60 amps

(Castro et al. 2010) where the catalytic activity per atom decreases due to the agglomeration of Cu nanoparticles at higher sputtering times.

Figure 3 presents the inactivation times for *E. coli* obtained by HIPIMS Cu samples at 6 amps when the sputtering has been applied between 2 and 21 s (Kusiak-Nejman et al. 2011). The bacterial inactivation takes place in the dark. Results taking 0.3 nm as the distance between Cu atoms in the Cu network and the thickness of an atomic layer ~0.2 nm when layers of 20 nm were deposited within 20 s (Fig. 2), about 100 layers with a content of 1×10^{17} atoms Cu/cm^2 were loaded on the polyester. This is a Cu deposition ratio of 5×10^{15} atoms/cm^2/s.

Above Fig. 2 shows *E. coli* inactivation within 10 min for samples prepared by DCMSP with a Cu content of 0.269%. Figure 1 shows the bacterial inactivation by DCMS prepared on samples loaded with 0.060% Cu in the dark within 120 min. The HIPIMS deposit Cu ions with ~30 eV compared with 5–15 eV for DCMS and energies up to 100 eV

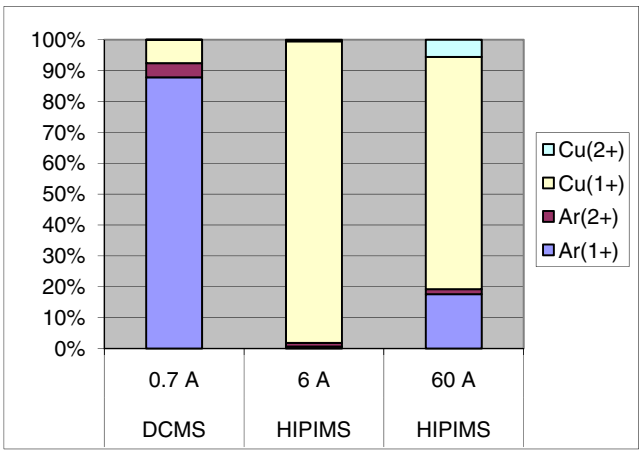

Fig. 5 Ar ion composition and Cu ion composition determined mass spectrometry in the gas phase of a DCMS and a HIPIMS sputtering chamber. For other details, see text

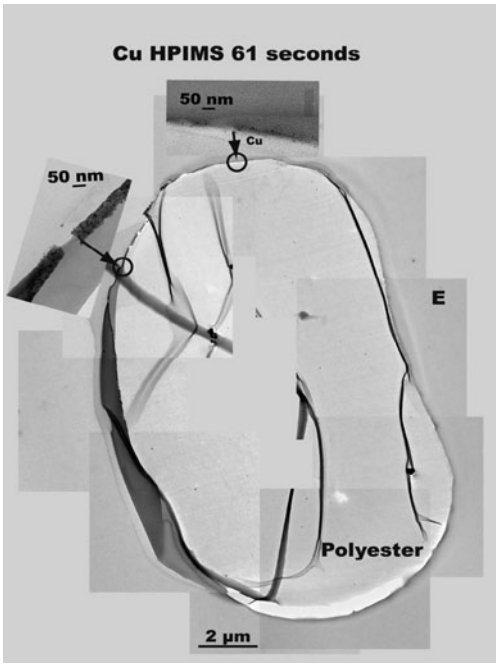

Fig. 6 Electron microscopy of an Ag-polyester fiber HIPIMS sputtered for 61 s at 60 amps. *E* stands for the epoxide used in the preparation of the sample

for DCMSP (Osorio et al. 2011). It seems that the deposition energy of the Cu ions impinging on the textile as shown in Fig. 2 was the controlling factor determining the bacterial inactivation kinetics (Mathews 1975).

Figure 4 presents the inactivation kinetics of *E. coli* mediated by Cu nanoparticulate films HIPIMS sputtered between 3 and 61 s at 60 amps. It is readily seen that as the HIPIMS sputtering increases the times needed to inactivate *E. coli* becomes shorter. The times of sputtering and the energy applied were different to the ones used in Fig. 3. The higher energies of polyester sputtered with 60 amps may promote a faster migration of the Cu particles compared to HIPIMS at 6 amps (Sarakinos et al. 2010). Also, a local softening of the fibers at the contact sites takes place at a higher sputtering energy, and this may play a significant role in the inactivation time of *E. coli* when sputtering with high currents as compared to lower currents due to the effect of higher temperatures available to the substrate (Perelshtein et al. 2009)

Cu ions and Ar ions composition sputtered by HIPIMS and DCMS derived from mass spectroscopy analysis Figure 5 presents the ion composition when sputtering from the same Cu target by DCMS and HIPIMS in Ar, derived from mass spectroscopy analysis. By inspection of Fig. 5, it is readily seen that the composition of the ions in the DCMS chamber gas phase was: 87% Ar^+, 5% Ar^{2+}, and 8% Cu^+. Low amounts of Cu^+ ions were found for the DCMS-sputtered samples in Fig. 5. The amount of Cu^+ ions increases with HIPIMS at 6 amps to reach 97% along 3% Ar^{2+}. Finally, at 60 amps, the composition of the gas phase is: 17% Ar^+, 3% Ar^{2+}, 75% Cu^+, and 5% Cu^{2+}. The HIPIMS runs show that with increasing current, the Ar^{2+} and the amount of Cu^{2+} in the gas phase increased.

During the magnetron sputtering chamber, the ionization $Ar \rightarrow Ar^+ + e^-$ leads in a subsequent step to the collision of the electron with Cu: $e^- + Cu^\circ \rightarrow Cu^+ + 2e^-$. The high-speed electron during the physical collision with the Cu kicks off a second electron leading to the Cu^+ ion. In the case of HIPIMS, the electron/ions in the chamber due to the higher ionization of the Cu ions reach most of the area of the polyester fiber compared to the case of DCMS sputtering. At 60 amps, the 2e− collected at the polyester release a higher energy than the energy released at 6 amps during the settling of the Cu^+ ions on the polyester (Mathews 1975). To compare the sputtering energies, 700 W were used in DCMS on a target 7.6 cm^2 in diameter with a current density of 16.7 mA/cm^2. The current densities with HIPIMS at 6 and 60 amps (peak current values) proceeded with high values of 103.4 and 1,034 mA/cm^2, respectively.

Electron microscopy of the Cu nanoparticulate films sputtered by HIPIMS Figure 6 shows the composite electron microscopy of Cu nanoparticulate films sputtered for 61 s at 60 amps. The fiber is presented in a 2-μm scale and the borders with the Cu nanoparticles were analyzed with a higher resolution (50-nm scale) along the perimeter of the fiber. The Cu layers vary between 10 and 35 nm depending

Table 2 C and Cu species on polyester Cu sputtered by HIPIMS for 61 s at 60 amps

Sample	C–C 284.6 eV	C–O 286.1 eV	O–C=O 288.6 eV	Cu_2O 932.3 eV	CuO 934.1 eV
Polyester blank	62.63	26.67	10.71		
Polyester+Cu, time 0	80.74	10.47	9.07	71.19	28.81
Polyester+Cu+bacteria, time 0	71.42	20.49	8.08	16.35	83.65
Polyester+Cu+bacteria (30 min)	62.78	27.18	8.28	29.97	70.03
Polyester+Cu+bacteria (60 min)	64.03	22.55	10.20	7.19	92.81
Polyester+Cu+bacteria (90 min)	60.07	31.39	7.38	6.08	93.92

of the area of the fiber being exposed directly or not to the axial direction of the plasma flux coming directly from the Cu target.

The Cu layer in the left upper corner in Fig. 6 shows a Cu particulate band with small Cu islands 5–10 nm size. The thick band is sputtered on the fiber when the plasma flux is aligned along the axial direction of the Cu target.

The Cu layer on the top of the polyester fiber shows a thin Cu particulate band with small Cu islands between 5 and 10 nm. In this case, the plasma flux reached the opposite side of the fiber.

We followed the distribution of Cu layers taken 12 EM plates in different zones of the polyester fiber perimeter. The Cu particles in the thicker and thinner band marked by arrows in Fig. 6 present similar particle size implying a similar Cu microstructure independent of the Cu layer thickness deposited on the polyester.

X-ray photoelectron spectroscopy experiments The polyester/Cu surface was followed as a function of *E. coli* inactivation time by XPS. Polyester/Cu samples sputtered for 61 s at 60 amps show a Cu2p doublet and the shake-up satellites CuO at 934.1 and 932.3 eV (Wagner et al. 1979).

Table 2 shows that at time 0, the majority of Cu exists as Cu_2O (71.2%) since the CuO content is only 28.8%. Contact with the bacterial suspension results in a significant oxidation of the Cu_2O to CuO (83.7%). During the bacterial oxidation, the CuO was reduced after 30 min to 70%. At longer bacterial inactivation times, the CuO oxidizes again increasing to ~94% up to complete bacterial inactivation within 90 min. At this point, polyester/Cu is ready to oxidize *E. coli* again. The results presented in Table 2 describe the variation of the Cu^+ and Cu^{2+} within the reaction time suggesting a complex redox mechanism during the *E. coli* inactivation. At the beginning of the *E. coli* inactivation, sputtering was observed to lead to the deposition of Cu(I)/CuO but later during the *E. coli* inactivation, the Cu(I) becomes (Cu II)/CuO.

The XPS C1s line shows three components: C–C aromatic at 284.6 eV, C–O at 286.1 eV, and O–C=O at 288.6 eV characteristic for the polyester-Dacron (polyethylene terephthalate, PET). There is a significant modification of the line at 288.6 eV after Cu deposition (spectrum b). A very broad peak with an additional component at around 287.5 eV suggests changes in the electrons distribution of the O–C=O group due to Cu deposition. This involves the partial reduction of carboxylic group O–C=O to carbonyl group C=O and has been reported previously by our laboratory (Dhananjeyan et al. 2001). The broadening of the O–C=O signal during *E. coli* inactivation is suggested to be due to the direct interaction of the surface Cu species with carboxylic groups. During the course of *E. coli* inactivation, the C1s line shows a different ratio between the carbon components at 286.1 and 288.6 eV.

4 Conclusions

This study presents the first report for HIPIMS Cu thin film deposition being effective in *E. coli* inactivation within reasonable times. The Cu ion sputtering energy is more important in the formation of a microstructure leading to short bacterial inactivation than the effect of (a) the target current, (b) the Cu ion density, and (c) the chamber geometry. The redox catalysis involving Cu^+/Cu^{2+} and the functionality of the C-intermediates during bacterial inactivation were both identified by XPS.

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