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Antimicrobial Cu-functionalized surfaces prepared by bipolar asymmetric DC-pulsed magnetron sputtering (DCP)

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ABSTRACT

Cu-cotton fabrics were functionalized by bipolar asymmetric DC-pulse magnetron sputtering (DCP). The DCP of Cu-particles on cotton proceeds at a higher energy than DC-magnetron sputtering (DC). The different sputtering mode showed effects on the structure of the Cu-film on the textile. The Cu-layer thickness was observed to be a function of DCP time being the rate of atomic deposition of 2.5×10^{15} atoms/cm^2 s at 300 mA. The fastest *Escherichia coli* inactivation was observed within 10 min when Cu was sputtered on cotton Cu for 60 s. This led to a film thickness of 30 nm (150 Cu-layers) with 1.7×10^{17} atoms/cm^2. The Cu-textiles became darker at longer sputtering times as detected by diffuse reflectance spectroscopy (DRS). By transmission electron spectroscopy (TEM), Cu-particles 35–50 nm in size were found and became more compact on the cotton surface as a function of deposition time. X-ray photoelectron spectroscopy (XPS) was used to determine the surface atomic concentration of O, Cu C, and N along the states of oxidation of the Cu-ions during the redox process leading to *E. coli* inactivation. The oxidation of the *E. coli* on the Cu-cotton surface was a function of reaction time and was monitored by the oxidation index of the carbon species on the fabric according to the ratio: (C–OH)/(C–C, C=C, C–H). The increase in hydrophobicity of the Cu-cotton was followed as a function of the contact angle and droplet residence time for different samples. The results obtained for the *E. coli* inactivation on the Cu-films are discussed suggesting a possible reaction mechanism.

1. Introduction

Cu has been known for a long time to have effective bactericide action [1,2]. More recently Cu-ions have been reported to be biocidal by binding to specific sites in the DNA [3] or by damage of the bacterial cell walls. In this later case the Cu-ions would enter into the cytoplasm causing membrane disruption [4]. Cu has also been shown to produce reactive oxygen species (highly oxidative radicals) leading to the damage of the iron-sulfur enzymes although the complete mechanism of bacterial inactivation has not been worked out. It is believed to proceed with a mechanism similar to Ag [5]. Current research in the field of antimicrobial surfaces focuses on the incorporation of Ag, Cu, Zn, and TiO_2 on medical devices, solid surfaces, textiles and thin polymers. These antimicrobial agents inactivate bacteria, *fungi*, viruses and *algae* due to the non-specific nature of the attack by the highly active metal/oxide nanoparticles on the cell wall proteins [6].

Conventional methods such as precipitation or ion exchange result in broad size distribution to deposit Ag, Cu bactericide metals on surfaces. Up to date sputtering techniques allows to produce and deposit thin film nanoparticles of Ag, Cu of a narrow size distribution presenting meaningful bactericide action [7]. The ways to increase and stabilize the antibacterial activity of Cu-surfaces is important in order to decrease or eliminate completely the costly nosocomial hospital infections (HAI) [8,9]. Towards this end, our laboratory has reported recently DC-magnetron sputtering of Cu on cotton surfaces with significant biocidal activity [10]. This study was undertaken since previous depositions with large surface BET Cu-powders on cotton led to non-uniform coatings with low adhesion although leading to the inactivation for *Escherichia coli* [11]. CuO with large surface area [12] and of Ag deposited by magnetron sputtering on cotton inactivated airborne bacteria efficiently [13]. Also Cu-TiO_2 sputtered films on glass show biocidal activity [14–16]. The use of sputtering has increased in the last

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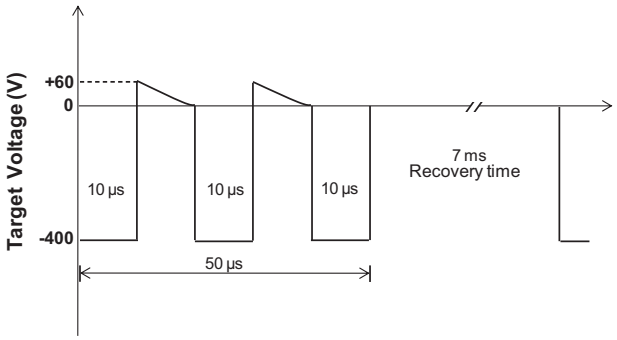

Fig. 1. Asymmetric bipolar DC-magnetron pulse. For other details see text.

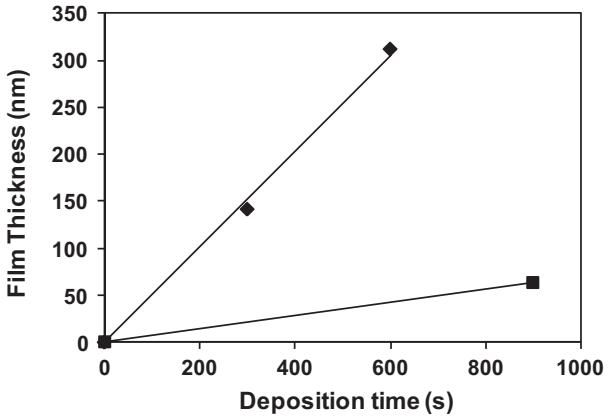

Fig. 2. Cu-layer thickness deposited by PMS as a function of time on Si-wafers. The lower trace corresponds to the thickness of the Cu-layers when using a PMS current of 50 mA and the upper trace corresponds to a PMS current of 300 mA.

decade for the deposition of metals and oxides along PVD for thin and thick film deposition [15,17].

This study addresses the pulsed DC-magnetron sputtering (DC) of uniform, dense Cu-layers mechanically durable and relatively well-adhered films at temperatures <100 °C. At present insufficient information is available showing the detailed structure and biocidal activity of Cu-films. The bactericide action of DCP deposited films occurs within several minutes (~10 min) and is much faster than in our last study on DC sputtered Cu-layers on cotton fabrics (~30 min), the subject investigated in this study is meaningful. The detailed description and characterization DCP deposited Cu-layers in relation to the biocidal activity is presented in this work. It is well known that the crystallization of the deposited metal depends on the energy delivered to it during the deposition/of the metal atom on the substrate (in our case cotton) [18]. Recently the DCP deposition of CrN films has been shown to proceed with a wide range of ion-energies. The distribution of electron densities were followed up to ~100 eV (with a small number of ions exceeding >100 eV) and a relatively high degree of ionization of the metal due electron densities of $\sim 10^{16}$ e^-/m^3. In the case of DC-magnetron sputtering, only ion-energies between 5 and 15 eV lead to a lower degree of ionization of the metal with electron densities of $\sim 10^{14}$ e^-/m^3 [19,20].

2. Experimental

2.1. Cu-magnetron sputtered deposition on cotton

DC sputtering was carried out in the sputtering chamber by means of a 5 cm diameter Cu-target plate bombarded by Ar-ions [10]. Applying a current of 300 mA needed a bias voltage of −400 V. DC pulse-magnetron sputtering 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) to accelerate the Cu-particles towards the substrate During DCP continuous pulses of 10 μs were applied, but with time the target gets overcharged and when this occurs, the unit tries three times to clear the charging arc with additional three pulses (see Fig. 1) before the power supply shuts down for 7 ms and turns on automatically after this recovery time. Fig. 1 shows schematically these additional pulses within 50 μs. 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, but as shown in Fig. 1, the PMS operation is bipolar asymmetric.

The Ar gas used in the sputtering chamber at 0.4 Pa and the sputtering current was fixed at 50 mA and 300 mA. In the case of 300 mA DCP, the voltage target applied was 430 V leading to a power density of about 6.6 W/cm^2.

Cotton was provided by Cilander AG, Herisau, CH-1109. The calibration of the Cu-coating was carried out up to 900 s for 50 mA and 600 s for 300 mA on Si-wafers. The film thickness was determined with a profilometer (Alphastep500, TENCOR). The calibration traces in Fig. 2 presented a ±10% range of variation or experimental error.

Taking 0.3 nm as the lattice distance of Cu-atoms about 10^{15} atoms/cm^2 can be estimated. Fig. 2 indicates for 50 mA a rate of deposition of 0.25×10^{15} atoms Cu/cm^2 s and for 300 mA a deposition rate of 2.5×10^{15} atoms Cu/cm^2 s. A higher Cu-deposition rate is due the higher current applied. Being an atomic layer ~0.2 nm thick, for a 60 s deposition a film thickness of 30 nm or 150 Cu-layers is deposited with 1.7×10^{17} atoms/cm^2.

2.2. X-ray fluorescence determination Cu-content on the cotton surface

The Cu-content of the cotton was evaluated by X-ray fluorescence. By this technique, each element emits an X-ray of a certain wavelength associated with its particular atomic number. The spectrometer used was RFX, PANalytical PW2400.

2.3. Diffuse reflectance spectroscopy of Cu-cotton surfaces (DRS)

The DRS spectra samples were measured using a Cary5 UV–vis–NIR spectrophotometer equipped with an integration sphere on 2 cm × 2 cm size samples.

2.4. High resolution transmission electron microscopy (HRTEM)

A Philips HRTEM CM 300 (field emission gun, 300 kV, 0.17 nm resolution) microscope and a Philips EM 430 (300 kV, LaB_6, 0.23 nm resolution) were used to measure the particles sizes of Cu-clusters. The textiles were embedded in epoxy resin (Embed 812) and the fabrics were cross-sectioned with an ultra-microtome (Ultracut E) up to a thin section of 70 nm. Magnification from about 6800× to 41,000× was used to identify the Cu-clusters and determinate the Cu-layer morphology.

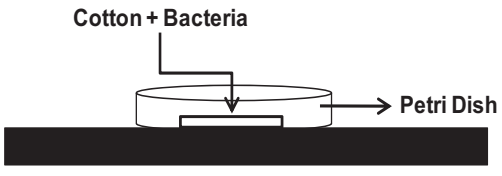

Fig. 3. Scheme of the experimental set-up to monitor the bacterial inactivation.

2.5. X-ray photoelectron spectroscopy (XPS)

An AXIS NOVA photoelectron spectrometer (Kratos Analytical, Manchester, UK) equipped with monochromatic AlK_α ($h\nu$ = 1486.6 eV) anode was used during the study. The kinetic energy of the photoelectrons was determined with the hemispheric analyzer set to the pass energy of 160 eV for wide-scan spectra and 20 eV for the case of high-resolution spectra. Electrostatic charge effect of the sample was overcompensated by means of the low-energy electron source working in combination with a magnetic immersion lens. The carbon C1s line with position at 284.6 eV was used as a reference to correct the charging effect. Quantitative surface composition was determined from peak areas using sensitivity factors [21,22]. Spectrum background was subtracted according to Shirley [23]. The etching of the sputtered Cu-cotton samples for 20 s was carried out by Ar^+-ions 5 keV reaching ~10 nm depth. The XPS spectra for the cu-species were analyzed by means of spectra deconvolution software (CasaXPS-Vision 2, Kratos Analytical, UK).

2.6. Contact angle measurements

The contact angle of cotton and sputtered Cu-cotton as a function of sputtering time were measured by means of a DataPhysics OCA 35 instrument following the Sessile's method for the analysis of water droplets by this technique.

2.7. Evaluation of bacterial inactivation of E. coli K-12 on Cu-cotton samples

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-cotton fabrics. The cotton fabrics were sterilized by autoclaving at 121 °C for 2 h. 20 μL 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) cotton fabric. The samples were placed on Petri dish provided with a top 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 was then 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. This was 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 were replicated for three times in the experimental set-up shown in Fig. 3.

3. Results and discussion

3.1. X-ray fluorescence of Cu-cotton sputtered samples

The Cu-content of the cotton sputtered samples was determined by X-ray fluorescence. The Cu-content (w/w) as a function of the PMS deposition times were: at zero s 0.0080%; at 4 s 0.048%; at 20 s 0.114%; at 40 s; 0.150% and at 60 s 0.269%. Ionic Cu-species will be described/identified in the XPS section in Fig. 7.

3.2. Diffuse reflection spectroscopy of Cu-cotton and color of the samples

Fig. 4 shows the increase in optical absorbance for Cu-cotton samples sputtered for 4 s, 40 s and 60 s. The wide spectral range in the visible region of CuO a p-type semiconductor with a band gap of 1.7 eV and a flat band potential of −0.3 V vs SCE (pH 7) [24]. Cu-cotton as seen in Fig. 4 is also a UV-shielding textile useful in some industrial application of fabrics.

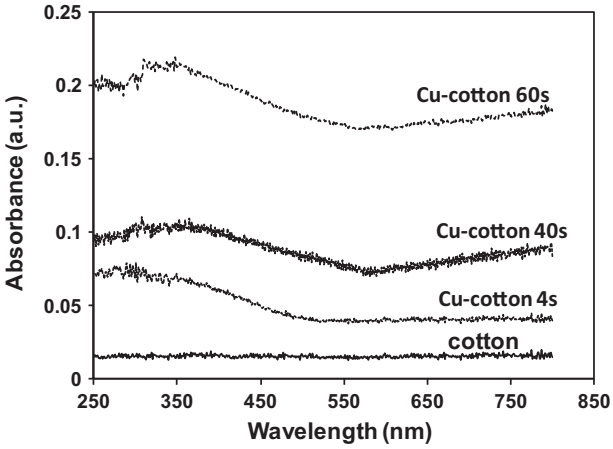

Fig. 4. Diffuse reflection spectra of Cu-cotton fabrics sputtered at different times.

Fig. 5 shows the cotton samples DCP sputtered with 300 mA for 0 s, 4 s, 20 s and 40 s. The cotton shows no color in the absence of Cu and a light grey-beige color appears at 4 s becoming progressively darker brown with a more brilliant metallic shade at 20 s and 40 s sputtering times. The darkening of the color is consistent with the increasing of Cu-content of samples as determined by X-ray fluorescence (see Section 3.1).

The particle size of the Cu-nanoparticles sputtered for longer times were observed to grow into bigger agglomerates (see Section 3.3 and Fig. 6a–c). The migration/aggregation of the sputtered particles on the cotton is driven by the high surface energy and leads to thermodynamically stable nanoparticles with a bigger size [18]. The growth of darker Cu-epitaxial film on the cotton takes place as the Cu-atoms diffuse anisotropically agglomerating as a function of the sputtering time. This is shown graphically in Fig. 5a–d. Repeated friction with paper or cloth did not smear the Cu-film out of the cotton.

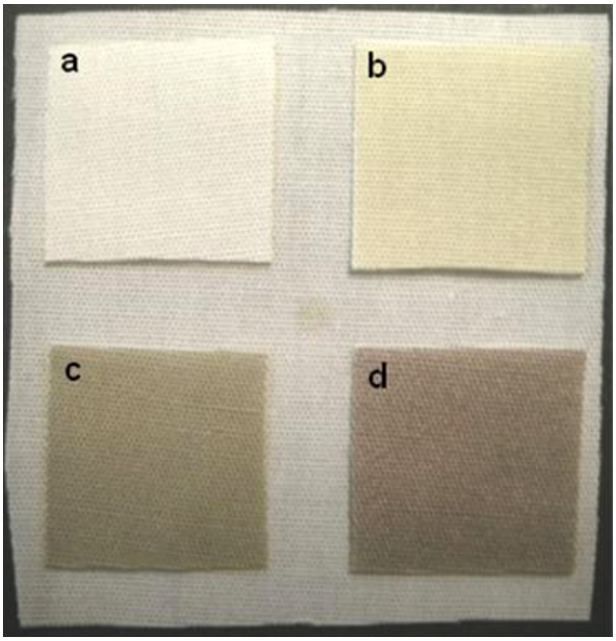

Fig. 5. Samples of Cu-cotton sputtered for: (a) zero time, (b) 4 s, (c) 20 s and (d) 40 s.

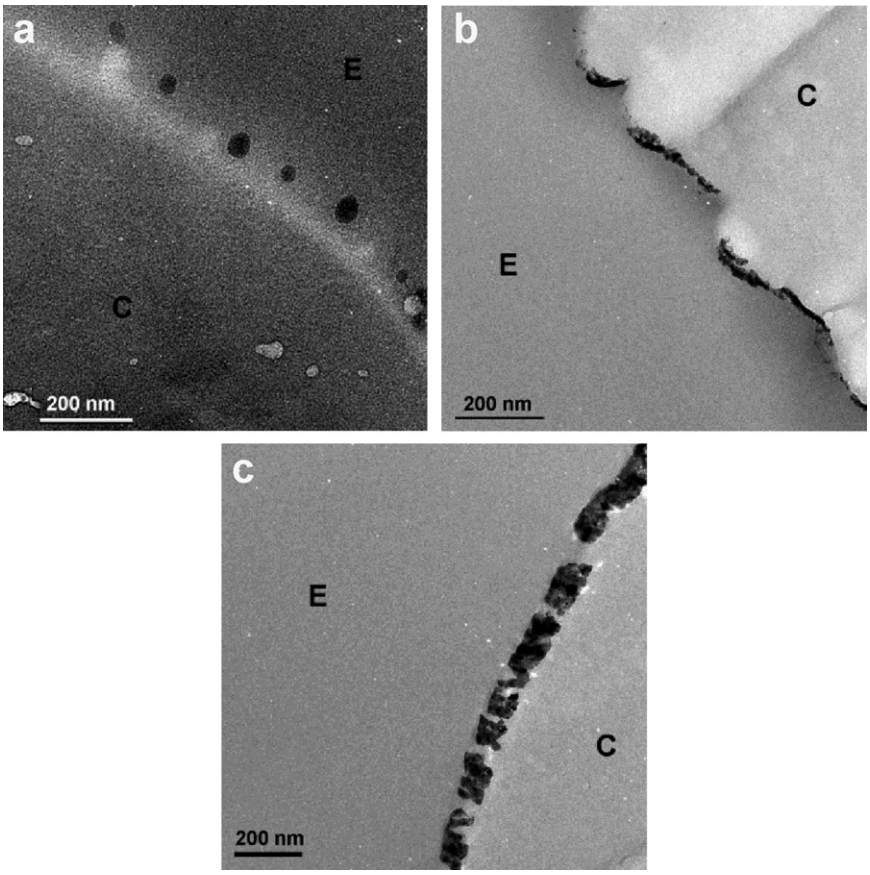

Fig. 6. Electron microscopy of Cu-cotton samples sputtered for: (a) 4 s, (b) 20 s and (c) 60 s.

3.3. High-resolution transmission electron microscopy (HRTEM) of Cu/CuO particles on cotton samples

Fig. 6a–c presents the HRTEM results for cotton samples showing the uppermost ten layers or ~2 nm. The C in these figures stands for "cotton" and E refers to "epoxide" used to prepare the samples for EM as described in the experimental part. Fig. 6a presents a low density of Cu-clusters on the cotton after sputtering for 4 s. Due to this low density of particles, a slow *E. coli* bacterial inactivation was observed in the dark as shown in Fig. 9. Particles shown in Fig. 6a, present an average size of ~50 nm. The Cu-clusters in the samples sputtered for 20 s (Fig. 6b) show an increased Cu-particle density consistent with an increased migration/agglomeration occurring at longer sputtering time. But still areas on the cotton fiber are observed not covered by Cu-nanoparticles. Almost complete epitaxial Cu-coverage on the cotton fiber is shown in Fig. 6c for sputtering times of 60 s. This sample provided the fastest inactivation of *E. coli* as shown in Fig. 9.

As the loading of Cu increases from 0.048% (4 s) up to 0.269% (60 s), the density of Cu nanoparticles increase and the catalytic activity also increases. This suggest that the added 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 a situation quite different to the one found with DC-sputtering [10] where the catalytic activity *per* atom decreases due to the agglomeration of Cu-nanoparticles at higher sputtering times. Therefore, the higher energies used in the PMS up to 100 eV seem to deposit Cu nanoparticles with a different structure/properties than the ones deposited by DC-magnetron sputtering at energies of 5–15 eV [19,20].

3.4. X-ray photoelectron spectroscopy of Cu-cotton samples (XPS)

Fig. 7 shows the binding energies (B.E.) for deconvoluted peaks for a Cu-cotton sample sputtered for 20 s for different *E. coli* inactivation times. The percentage of Cu-ionic species as a function of bacterial inactivation time is shown in Table 1. The variation of the percentage of the Cu-ionic species in Fig. 7 as a function of time shows that we are in the presence of a redox process involving Cu-species and *E. coli* during bacterial inactivation. Cu^{1+}/Cu^{0} decreases with time. This is in agreement with the results reported recently for *E. coli* inactivation by Cu-species involving XPS work [10,13]. The envelope Cu^{1+}/Cu^{0} component at 933.1 eV could not be unambiguously deconvoluted without introducing a large approximation when identifying the peaks for Cu^{0} and Cu^{1+}(932.8 eV) [21,22]. The Cu^{1+}/Cu^{0} followed by a decrease up to 60 min when the *E. coli* inactivation is completed (see Fig. 9). The position of the Cu^{2+} peak has been reported at 934.2 eV.

Table 2 shows the values found the species Cu^{1+}/Cu^{0} after etching with 5 keV Ar-ion. These Cu^{+}/Cu^{0} equilibrium changes with time at 6 nm depth or ~30 atomic layers. Favorably protected Cu-ionic clusters are seen to vary in composition inside the cotton fabric intervening in the *E. coli* inactivation. The Cu^{2+}-content decreases as the time of *E. coli* inactivation progresses.

Table 1
Percentage of Cu-ionic species cotton as a function of *E. coli* inactivation time.

Contact time (min)	Cu^{1+}/Cu^{0}	Cu^{2+}
0	5.07	3.96
10	2.00	6.77
60	1.58	4.50

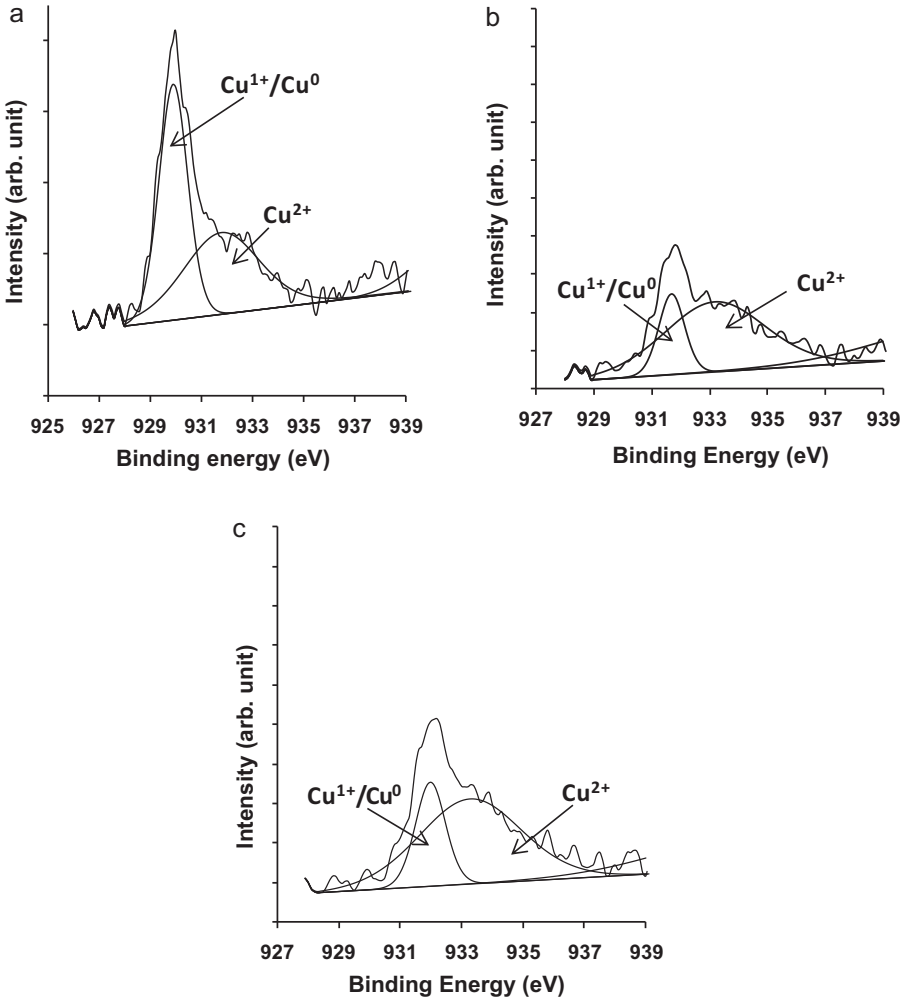

Fig. 7. XPS spectra of Cu-cotton samples showing the deconvoluted peaks for the Cu-ionic species as a function *E. coli* inactivation time: (a) $t = 0$ min, (b) $t = 10$ min and (c) $t = 60$ min.

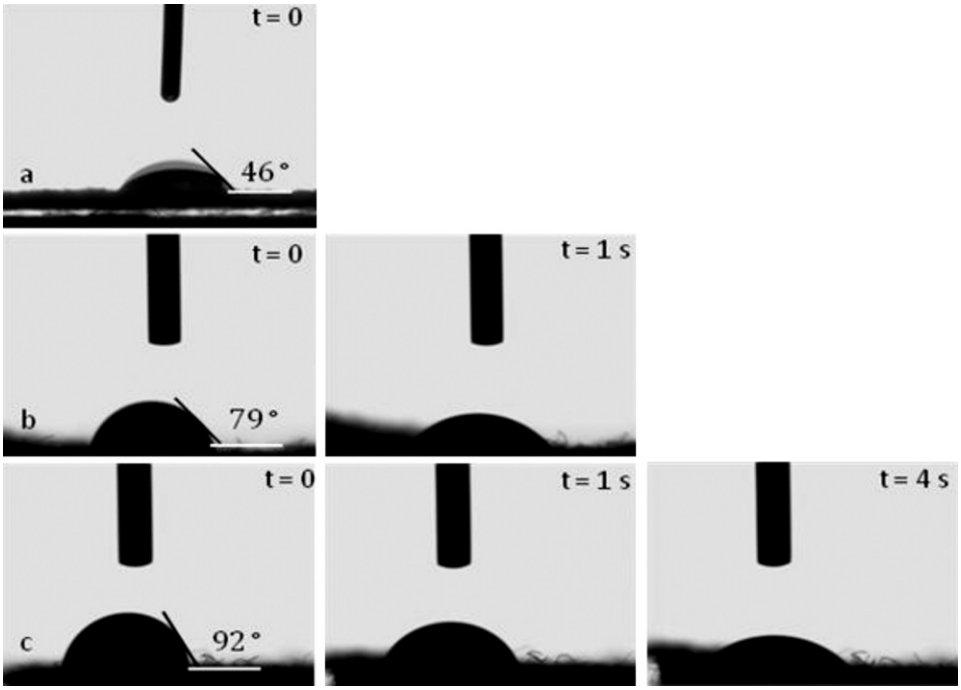

Fig. 8. Water droplet contact angle as a function of the droplet residence time on Cu-cotton samples: (a) cotton alone, (b) sputtered for 20 s and (c) sputtered for 60 s.

Table 2
Percentage of Cu-ionic species cotton as a function of *E. coli* inactivation time. Etching depth of 6 nm.

Contact time (min)	Cu^{1+}/Cu^0	Cu^{2+}
0	15.0	5.42
10	18.6	4.71
60	14.1	3.79

Table 3
Ratio of oxidized and reduced carbon species on the Cu-cotton as a function of *E. coli* inactivation time.

Contact time (min)	$C_{C-OH}/C_{C-C,C=C,C-H}$
0	0.043
10	0.436
60	0.410

Table 4
Percentage of the surface atomic concentration in Cu-cotton as a function of *E. coli* inactivation time.

Contact time (min)	O	Cu	C	N
0	21.2	9.03	69.7	0.00
10	21.8	8.77	67.9	1.50
60	17.0	5.96	76.1	0.90

Table 3 shows the increase in the ratio of the oxidized species $(C_{C-OH})/(C_{C=C}, C_{C=C}, C_{C-H})$ to the reduced species on the cotton topmost layers as the *E. coli* inactivation proceeds to completion within 60 min. The XPS signals have been followed as a function of *E. coli* time for C–OH (B.E. at 285.9 eV) and (C–C, C=C, C–H) as the reduced forms of C with B.E. 285.0 eV [21,22]. The resolution of the B.E. in our XPS instrument is of 0.1 eV.

Table 4 shows the surface atomic concentration of the Cu-cotton fabrics as a function of the *E. coli* inactivation time. At time zero, it is seen that the composition of the upper layers consisted entirely of O, Cu, C, and N. The Cu-content decreases with time due to the increased coverage of C on the surface of the film left by the dead bacteria within 60 min, the time of the inactivation process.

3.5. Contact angle measurements and droplet adsorption times

Fig. 8 presents the results of the contact angle measurements. Fig. 8a shows a contact angle of 46° for bare cotton revealing a hydrophilic surface and the density is so low that the water penetrates easily this fabric. For Cu-cotton samples sputtered for 20 s the contact angle shows an increase to 79° in Fig. 8b. This shows that the deposition of Cu well increases the hydrophobic character of the cotton surface since the water droplet is still visible at 1 s. The increase in hydrophobicity is readily seen for Cu-sputtered samples for 60 s in Fig. 8c where at time zero the contact angle was 92°. Concomitantly, the adsorption of the water droplet decreases being the water droplet still visible at 4 s. The void area inside the cotton fabrics is reduced during the Cu-sputtering process decreasing the water penetration and enhancing the hydrophobicity of the cotton fabrics. The increase in the droplet contact angle in sputtered samples is accompanied by an increase in roughness of the Cu-cotton samples favors the adsorption and stabilization of Cu-ions on the Cu-sputtered layers. This effect increases with the number of Cu-layers attained at longer sputtering times and this important effect on *E. coli* inactivation is shown next in Fig. 9.

3.6. E. coli bacterial inactivation on Cu-cotton

Fig. 9 presents the results of the *E. coli* inactivation by PMS bipolar asymmetric Cu-sputtering of the cotton samples. Practically no *E. coli* inactivation was observed in the dark for cotton samples. But for Cu-cotton loaded samples bacterial inactivation is seen to be significant as reported recently in the dark for CuO suspensions [13]. The Cu-loaded samples sputtered for 20 s, 40 s and 60 s showed an increased bactericide activity in the dark as a function of sputtering time leading to a more favorable *E. coli* inactivation. We suggest that the ROS of *E. coli* was modified by interaction with Cu^{2+}/Cu^{1+} as suggested by reactions (1) and (2):

$$Cu^+ + O_2^{\bullet -} \rightarrow Cu^0 + O_2 \quad (1)$$

$$Cu^0 + O_2 \rightarrow Cu^+ + O_2^{\bullet -} \quad (2)$$

since H_2O_2 adsorbs on Cu/CuO, two possibilities exists for peroxide decomposition [25,26]

$$H_2O_2 + Cu \rightarrow HO^- + OH^0 + Cu^+ \quad (3)$$

$$H_2O_2 + Cu^+ \rightarrow HO^- + OH^0 + Cu^{2+} \quad (4)$$

The Cu^{2+} as Fe^{3+} is able to enhance the ROS formation via Fenton like reactions (4) and (5) [27]

$$Cu^{2+} + e_{cb}^- \rightarrow Cu^+ \quad (5)$$

or by a two electron transfer from Cu^{2+} leading to Cu^0 atoms

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \quad (6)$$

The Cu-atoms then coalesce to Cu^0 nano-particles settling in the Cu-network of the cotton with $E_{redox} = -0.34$ V vs. NHE [26].

In Fig. 9, electron transfer from the Cu to *E. coli* seems to proceed. This transfer relates to different structures in the Cu-crystals in

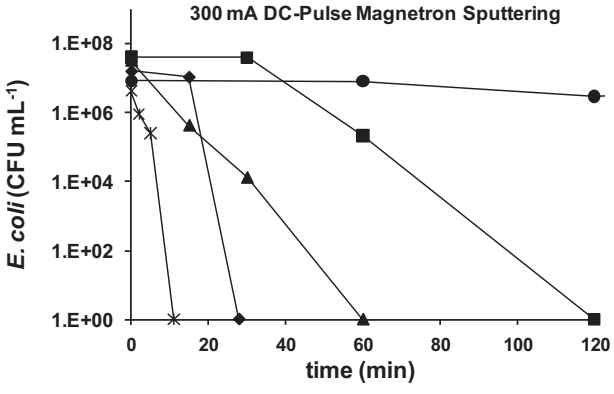

Fig. 9. *E. coli* inactivation by Cu-cotton samples in the dark. Cotton alone (●); 4 s (■); 20 s (▲); 40 s (♦); 60 s (×).

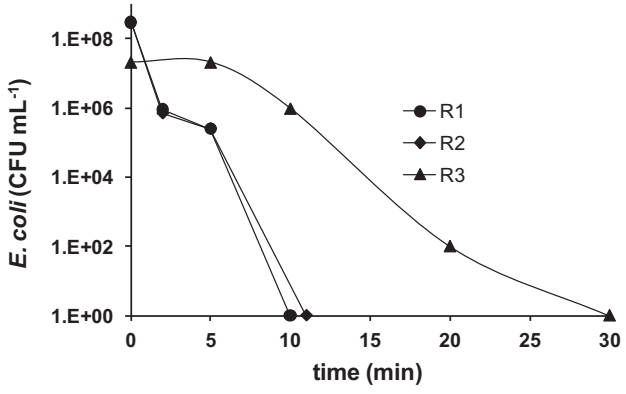

Fig. 10. Recycling of the Cu-cotton samples sputtered for 60 s during *E. coli* inactivation. R1, R2 and R3 refer to the first, second and third recycling of the same Cu-cotton samples adding each time a fresh sample of *E. coli* to be inactivated.

terms of spatial separation of redox sites having a different migration of electrons from these Cu nano-particles deposited at the DCP sputtering energies [19,20].

3.7. Recycling of Cu-cotton samples during E. coli inactivation

Fig. 10 presents the *E. coli* inactivation by Cu-cotton sputtered samples for 60 s. It is readily seen that the first two recycling proceed within 10 min but the third recycling becomes longer. After each recycling the samples were thoroughly washed with ultrapure water and dried at room temperature before adding the new bacterial charge to be inactivated. Experiments are under way to increase the adhesion of Cu on the cotton and the results will be reported in the near future.

4. Conclusions

- The results shown for Cu-layers on cotton show that bipolar asymmetric operation of the pulsed magnetron sputtering (DCP) depositing Cu on cotton accelerates the Cu-cotton fabric biocide action compared to DC-sputtering as reported recently by our laboratory [10]. This effect is probably due to the formation of different microstructure/properties of the Cu nano-particles on the cotton.
- Applying 300 mA DCP for 4 s, the threshold loading of Cu necessary to induce bactericide action in the Cu-cotton fabrics was 0.048% wt Cu/wt cotton with a loading of 10^{16} atoms/Cu/cm^2 and an equivalent thickness of about 1.0–1.2 nm or 5–6 Cu-layers.
- Modification of the cotton by Cu-deposition changes the surface from hydrophilic to increasingly hydrophobic. The Cu-loaded cotton deposited shields the UV-light and becomes an effective antimicrobial agent.

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