



## Structure–reactivity relations for DC-magnetron sputtered Cu-layers during *E. coli* inactivation in the dark and under light

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### ARTICLE INFO

#### Article history:

Available online 3 July 2010

#### Keywords:

Sputtering  
Cotton  
*E. coli*  
Cu-ionic  
Etching  
XPS

### ABSTRACT

This study addresses unreported features for Cu DC-magnetron sputtering on cotton mediating inactivation of *Escherichia coli* K12 (from now on *E. coli*). In-depth profile for the different Cu-species inside the cotton fibers was determined by 5 keV Ar<sup>+</sup> etching. Sputtering for 40-s deposited  $4 \times 10^{16}$  atoms Cu/cm<sup>2</sup> (taking  $\sim 10^{15}$  atoms/cm Cu per atomic layer) and this was the threshold amount of Cu necessary for complete bacterial inactivation. This is equivalent to a Cu-loading of 0.060% w/w or 3 nm/15 atomic layers. The inactivation of *E. coli* was attained within 30 min under visible light (1.2 mW/cm<sup>2</sup>) and within 120 min in the dark. XPS identified the Cu-species on the cotton as a function of the sputtering time. For a longer sputtering 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. This suggests that Cu-ionic species play a key role *E. coli* inactivation. The 40 s sputtered samples present the highest amount of Cu-sites held in exposed positions interacting on the cotton surface (or inside the cotton) with *E. coli*. Confocal microscopy shows the higher rugosity of Cu-cotton fibers compared to bare cotton fibers. The Cu-clusters were observed to be  $\sim 50$  nm after 40 s DC-magnetron sputtering and presented a wide size distribution. Cu DC-magnetron sputtering leads to thin metallic semi-transparent grey-brown Cu-coating presenting a moderate hydrophobic behavior as determined by contact angle measurements.

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### 1. Introduction

The manufacturing of high value added products such as bactericide textiles has increased rapidly in the last few years [1,2]. Cu-particles are used for their catalytic and bactericide properties. This development also opened new interest in the pre-treatment or activation of textiles to fix metal/oxides by: RF-plasma, Vacuum-UVC light [3,4] and corona discharge [5]. Bactericide textiles have been developed and intensively investigated recently by Daoud et al. [6,7].

The bactericide properties of Cu have been known for some time and described in their mechanistic features [8,9]. Recently, Borko and Gabay [10–12] have reported Cu-textiles and composite materials presenting antiviral, algicide and fungicide properties that sustain washing cycles loaded with CuO 1%. These textiles

have been reported to be effective against *E. coli*, *Staphylococcus aureus* and the fungi *Candida albicans* and were effective against other infections being also safe to humans and not causing skin irritation when externally applied.

Our group has reported Cu/CuO to be effective in the degradation of organic pollutants in the dark or light [13,14]. Recently, our Laboratory has also shown that large surface area Cu-suspensions were effective in *E. coli* inactivation in the dark and under visible light [15].

The present study addresses: (a) the relation between structure and reactivity of the Cu-clusters deposited by sputtering on cotton towards the inactivation of *E. coli* focusing in the threshold of the Cu-layers necessary to inactivate *E. coli* within acceptable times, (b) the identification if the Cu-ions on the cotton textile intervening in the *E. coli* inactivation by XPS, (c) the determination of the topography of Cu-cotton fabrics compared to cotton alone by confocal microscopy, (d) the quantitative increase in hydrophobicity of the Cu-cotton as a function of Cu-loading compared to bare cotton samples, and finally (e) the increase in density of the Cu-clusters on the cotton as a function of Cu-sputtering time.

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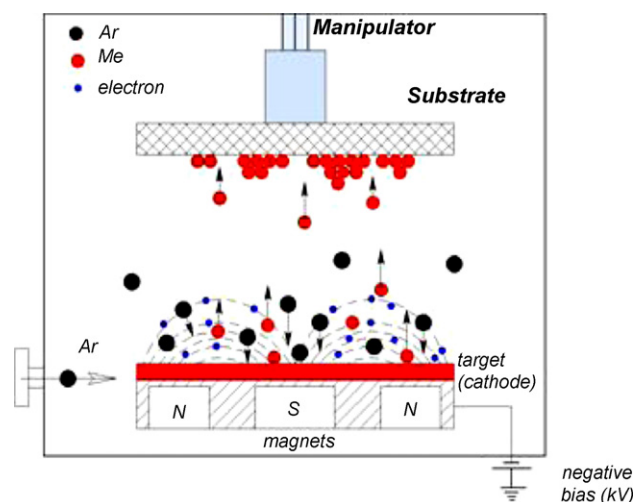


Fig. 1. Schematic diagram of a DC-magnetron sputtering unit.

## 2. Experimental

### 2.1. Cu deposition on cotton sample

In Fig. 1 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. Under these conditions Cu/Cu-ions reaching the target have such a high energy content that they penetrate more than ~10 nm or the equivalent of about 50 atomic layers inside the cotton network [16]. The adhesion of Cu to the cotton (ex Cilander AG, Herisau, CH-1109, 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 [17]. 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. This is shown in Fig. 2. Errors bars in Fig. 2 were obtained calculating for each deposition time the standard deviation and from this the standard error is reported in the bars of Fig. 2. The film thickness was determined with a profilometer (Alphastep500, TENCOR). A stylus, loaded with 4 mg and a tip radius of 5  $\mu\text{m}$  probed the film surface. The stylus is calibrated electrically putting the equivalent weight of 4 mg.

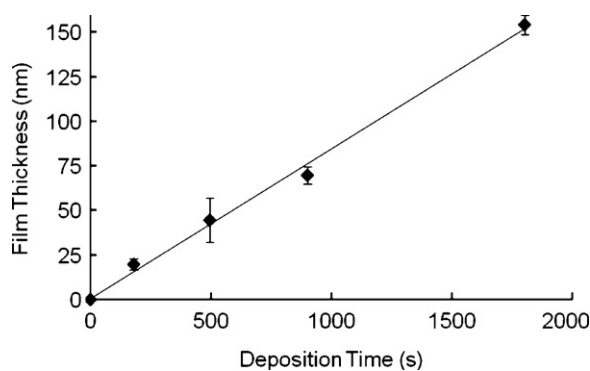


Fig. 2. Increase in the Cu-thickness during DC-magnetron sputtering with deposition time on silica slides.

### 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. Evaluation of the bacterial inactivation of *E. coli* K12

The bacterial strain *E. coli* K12 was inoculated in 5 ml of Luria Bertani solution and grown during 8 h at 37 °C with constant agitation under aerobic conditions. Aliquots of the culture were inoculated into a fresh medium and incubated aerobically at 37 °C for 15 h. At the stationary growth phase, bacteria cells were collected by centrifugation at 500  $\times g$  for 15 min at 4 °C and the bacterial pellets were washed three times and re-suspended in a NaCl/KCl solution. Cell suspensions were diluted with a saline solution with 0.75% NaCl and KCl 0.08% to allow the storage of the bacteria without osmotic stress [18].

The bactericide activity of cotton/CuO was tested on *E. coli*. The cotton samples were autoclaved at 121 °C for 2 h before the bacterial testing to avoid interference of other bacteria/microorganisms present in the laboratory. Then, 20  $\mu\text{l}$  aliquots of the culture in NaCl/KCl solution were placed on the cotton/CuO and control samples. The inactivation of *E. coli* using cotton alone was considered as control samples under light or in the dark. The samples were placed on Petri dish to prevent medium evaporation and after 5 min the sample was transferred to 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  $\mu\text{l}$  of each dilution was spread on the nutrient agar plate. Agar plates were incubated for 37 °C for 24 h before counting the CFU.

### 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<sub>6</sub>, 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 (Ultra-cut E) to a thin section of 50–70 nm. Magnification from about 6800–41,000 $\times$  was used to identify the Cu-clusters and determine the Cu-layer morphology.

### 2.5. Confocal microscopy

The confocal microscopy used a Carl Zeiss LSM 710 microscope. The topography of the micron range fibers was observed reflection mode. The system consists of a camera head and monitor that can detect signals at any point of the image. The surface was scanned with a 6 mW He–Ne laser. The reflected light by the sample comes back and is detected to register and store the signal using two lenses in a way that the plane of the image due to the first lens overlaps with the plane of the second lens allowing the analysis of the surface image.

### 2.6. Irradiation of Cu-cotton samples during the inactivation of *E. coli* K12

The irradiation of the Cu-cotton samples was carried out in a cavity provided with a tubular Osram Lumilux T8-L18W (ex Winterthur, Switzerland) actinic lamp having a visible emission spectrum between 400 and 500 nm as shown in the inset to

Fig. 4 with an integral output of  $1.2 \text{ mW/cm}^2$  (Winterthur, Switzerland).

### 2.7. X-ray photoelectron spectroscopy (XPS)

An AXIS NOVA photoelectron spectrometer (Kratos Analytical, Manchester, UK) equipped with monochromatic  $\text{AlK}_{\alpha}$  ( $h\nu = 1486.6 \text{ eV}$ ) anode was used during the study. The kinetic energy of the photoelectrons was determined with the hemispheric analyzer set to the pass energy of  $160 \text{ eV}$  for wide-scan spectra and  $20 \text{ eV}$  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  $\text{C1s}$  line with position at  $284.6 \text{ eV}$  was used as a reference to correct the charging effect. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and spectrometer transmission function [19,20]. Spectrum background was subtracted according to Shirley experimentally determined sensitivity factors and spectrometer transmission function [21]. The etching of the sputtered Cu-cotton samples (40 and 180 s) was carried out by  $\text{Ar}^+$ -ions  $5 \text{ keV}$  reaching  $\sim 10 \text{ nm}$  depth. The XPS spectra were analyzed by means of spectra deconvolution software (Vision 2, Kratos Analytical, UK) to assign the XPS bands for  $\text{Cu}^0$  and the Cu-ionic species on the cotton.

### 2.8. 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.

## 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  $\text{CuO}$  content w/w as a function of the sputtering time was:  $0 \text{ s } 0.0086\%$ ; at  $20 \text{ s } 0.042\%$ ; at  $40 \text{ s } 0.060\%$ ; at  $90 \text{ s } 0.135\%$  and at  $180 \text{ s } 0.294\%$ . Ionic species will be identified and described in the XPS section in Fig. 6.

Deposition times of 20, 40, 90, 180 and 360 s lead to Cu-layers of 1.5, 3.0, 7.8, 16 and  $28 \text{ nm}$  thickness on the cotton surface. This is shown in Fig. 2. The coating deposition rates were obtained depositing the sputtered cotton layers on a glass slide mounted on the substrate holder. Since one atomic layer consists of about  $10^{15}$  atoms and in Fig. 2 it is seen that  $10 \text{ nm}$  were sputtered in  $130 \text{ s}$ , it follows that the atomic rate deposition for Cu on cotton was  $7.7 \text{ atoms/cm}^2/\text{s}$ .

### 3.2. Deposition of Cu on cotton

Fig. 3 shows the cotton samples sputtered for 20, 40 and 180 s. The cotton shows no color in the absence of Cu-sputtering and a light grey-beige color appears at 20 s becoming progressively darker brown with a more brilliant metallic shade at 40 and 90 s sputtering times. The darkening of the color is consistent with the increasing of Cu-content of samples was determined by X-ray fluorescence (Section 3.1). The Cu-clusters sputtered on the cotton becomes progressively more abundant and agglomerate into bigger units as the sputtering time increases leading to darker epitaxial films as more Cu-atoms/ions diffuse anisotropically on the cotton surface (Fig. 3a–d). The adhesion of the Cu on the cotton (ex Cilander AG, Herisau, CH-1109, Switzerland) was strong.

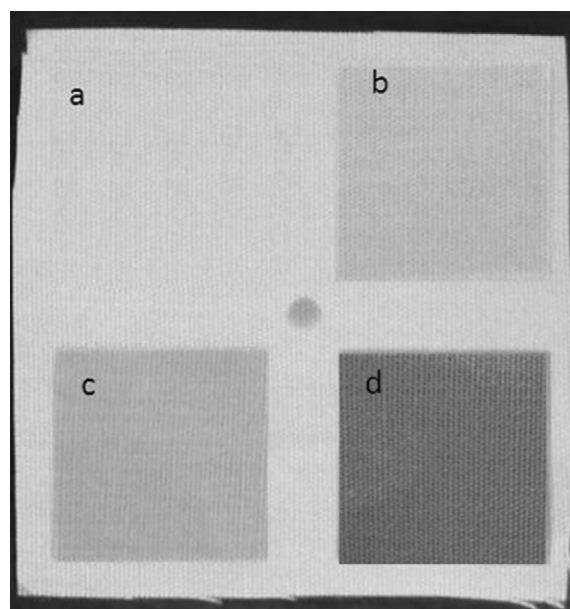


Fig. 3. DC-magnetron sputtered cotton fabrics: (a) cotton alone, time zero (b) 20 s, (c) 40 s, and (d) 180 s.

Friction with paper or cloth did not allow smearing of the Cu-coating.

### 3.3. *E. coli* bacterial inactivation in the dark and under low intensity visible light

Fig. 4 shows the inactivation of *E. coli* on Cu-sputtered samples. Cotton by itself did not inactivate the *E. coli*. The 40-s Cu DC-sputtered samples in the dark lead to complete bacterial inactivation within 120 min and within 30 min under low intensity visible light with  $\sim 1\%$  of the full solar light irradiation ( $\text{AM1}$ ) as used in Fig. 4. Sputtering times of 40 s lead to the threshold Cu-concentration of  $0.060\% \text{ w/w}$  necessary to completely inactivate *E. coli* within reasonable times. The sputtering for 180 s also lead to complete bacterial inactivation within 30 min under light and 120 min in the dark. But the sample sputtered for 180 s had a Cu-content of  $0.294\% \text{ w/w}$ , about 5 times above the threshold Cu-concentration. This shows that  $\text{Cu}^0$  is not the main species leading to bacterial deactivation, since the bacterial inactivation time was

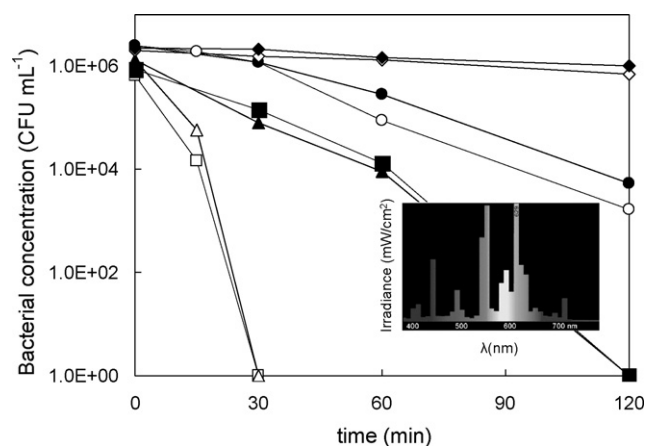
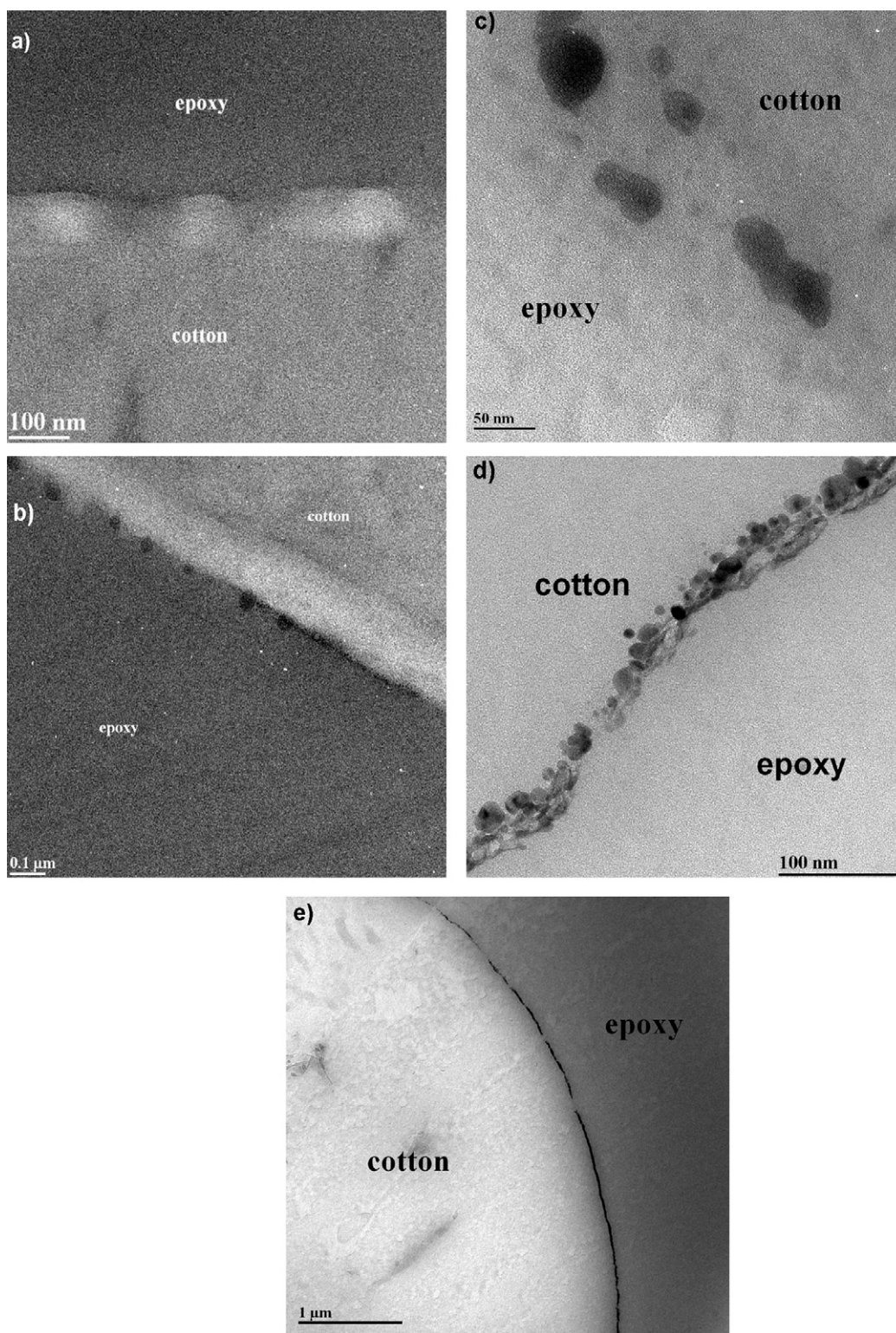


Fig. 4. *E. coli* inactivation for cotton: light ( $\diamond$ ), dark ( $\blacklozenge$ ) and Cu DC-magnetron sputtered cotton samples at times: 20 s dark ( $\bullet$ ), light ( $\circ$ ); 40 s dark ( $\blacksquare$ ), light ( $\square$ ); 180 s dark ( $\blacktriangle$ ), light ( $\triangle$ ). The spectral distribution of the visible light source used of  $1.2 \text{ mW/cm}^2$  is shown in the inset.





**Fig. 5.** Complete view by electron microscopy of the epitaxial covering of a Cu-cotton fiber by DC-magnetron sputtering. (a) Electron microscopy of cotton alone, (b) electron microscopy of Cu-cotton DC-magnetron sputtered for 20 s, (c) electron microscopy of Cu-cotton DC-magnetron sputtered for 40 s, and (d) electron microscopy of Cu-cotton DC-magnetron sputtered for 180 s.

the same in the dark and under light for samples sputtered at 40 and 180 s. The sputtering time of 40 s seems to produce the most favorable structure-reactivity for the Cu-cotton samples leading to the shortest *E. coli* inactivation time. Longer Cu-sputtering times did not lead to a shorter *E. coli* inactivation kinetics as shown in Fig. 4.

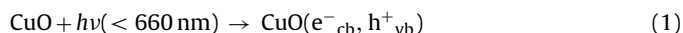
During *E. coli* inactivation the bacterial solution penetrates the hydrophilic fibers entering the void area in the cotton fabric. The bacterial inactivation of the Cu-cotton presents two distinctive features: (a) in dark processes the dispersion of Cu-clusters seems to be a controlling factor (see Sections 3.4 and 3.5 below) and (b) etching-depth experiments in Table 1 show different depths for the

**Table 1**Percentage of Cu-ionic species in the sputtered cotton for 40 and 80 s, etched with 5 keV Ar<sup>+</sup>-ions as a function of etching-depth.

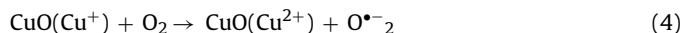
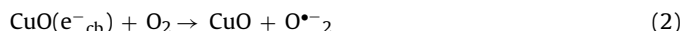
Etched depth (nm)	40 s			180 s		
	Cu(I)/Cu(0)	Cu(II)	Cu(III)	Cu(I)/Cu(0)	Cu(II)	Cu(III)
0.0	15.3	6.0	–	27.0	2.7	–
4.0	6.4	4.5	–	41.1	9.5	4.8
6.0	6.9	1.0	0.4	28.0	6.7	5.2
8.0	4.7	2.3	–	17.3	14.3	–

Cu-cluster deposition in the cotton fabric. The depth profile experiments carried out with Ar<sup>+</sup> sputtering were carried out for several minutes and the penetration depth reported in Table 1 was referenced by the known rate for Ta of 15 atomic layer/min or ~30 Å [19,20]. Due to the high energy of the impinging Cu-atoms/ions on the cotton, the Cu-ions penetrated up to 8 nm at 40 s sputtering times. Sputtering times of 180 s deposited Cu at deeper levels than samples sputtered for only 40 s on the cotton as reported in Table 1.

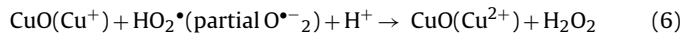
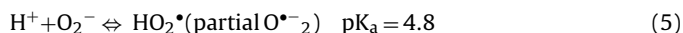
The mechanism of bacterial inactivation under light is suggested to follow the CuO semiconductor mechanism active under light in chemical reactions [14]. Cu forms CuO in the contact with air ((O<sub>2</sub>) in the net sense) and the acceleration of the bacterial inactivation of *E. coli* under light with respect to dark inactivation can be understood by the semiconductor behavior of CuO under light. The semiconductor character of CuO has been recently described [14,15]. Under irradiation CuO leads to surface oxidative radical formation:



The  $e^-_{\text{cb}}$  in Eq. (1) is produced from the CuO (p-type) with band-gap energy of 1.7 eV, a flat-band potential of –0.3 V SCE (pH 7) and a valence band at +1.4 V SCE [14]. The electron–hole pair is formed with photon energies exceeding the band-gap of CuO. The excited electron could either react (a) directly with the O<sub>2</sub> forming O<sup>•–</sup><sub>2</sub> (reaction (2)) or by (b) reducing the Cu<sup>2+</sup>-lattice to Cu<sup>+</sup> leading to the ensuing reactions (3) and (4) with formation of O<sup>•–</sup><sub>2</sub> radicals:



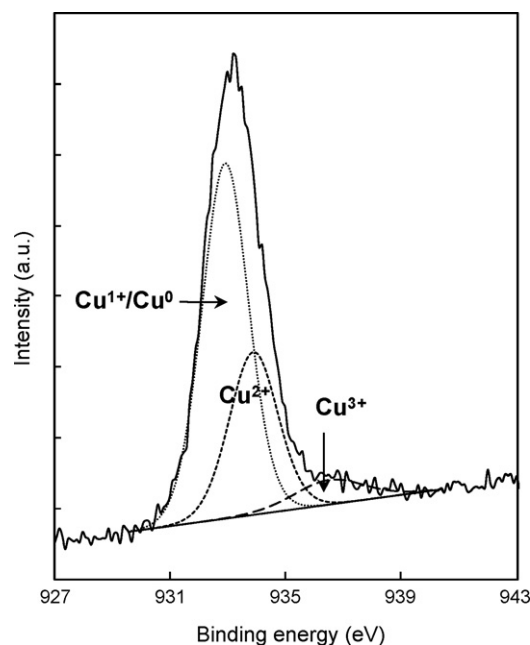
Eq. (5) shows that the equilibrium between H<sup>+</sup> and O<sup>•–</sup><sub>2</sub> leads to the formation of the HO<sub>2</sub><sup>•</sup> radical. The HO<sub>2</sub><sup>•</sup> in Eq. (5) generates H<sub>2</sub>O<sub>2</sub> adsorbed on CuO (see Eq. (6))



with  $k_8 = 0.6\text{--}2.3 \text{ M}^{-1} \text{ s}^{-1}$  [24].

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

Fig. 5a presents the HRTEM results for cotton samples. In this HRTEM the epoxide and cotton presented the same contrast and the particles observed in Fig. 5a–d were observed in the first 10 cotton layers or within 2 nm. Fig. 5b presents the low density Cu-clusters on the cotton after sputtering for 20 s. With this density of particles, no bacterial inactivation was observed under light or in the dark. A more detailed view of the 40 s sputtered particles is shown in Fig. 5c, presenting an average size of 50 nm. The Cu-clusters in the 180 s sputtered cotton (Fig. 5d) show an increased Cu-particle density consistent with an increased sputtering time [22,23]. The epitaxial Cu-coverage of the cotton fiber is shown in Fig. 5e.



**Fig. 6.** XPS spectra of Cu DC-magnetron sputtered cotton showing the deconvoluted peaks for the Cu-ionic species. For other details see text.

As the loading increases from 0.060% Cu w/w for the 40 s sample to 0.294% Cu w/w for the 180-s sample, the density of the clusters increase but the catalytic activity per exposed atom decreases due to this agglomeration process. Both samples report the same catalytic performance in the dark (120 min) and under light (30 min) for complete *E. coli* inactivation (Fig. 4). This suggests that the 40 s sputtered sample presents the highest amount of Cu-sites held in exposed positions on the surface or inside the cotton able to interact with *E. coli*. This is the optimal ratio of Cu-loading/cluster size for *E. coli* inactivation.

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

Table 2 shows the surface composition of the Cu-cotton fabrics as a function of the sputtering time. By inspection of Table 2, it is readily seen that the composition of the upper layers of Cu-sputtered cotton consisted entirely of O, Cu, C, N. Fig. 6 shows the XPS spectra of the deconvoluted Cu-doublet analyzed in terms of the Cu<sup>0</sup>/Cu<sup>1+</sup>, Cu<sup>2+</sup> and Cu<sup>3+</sup> components. The envelope Cu<sup>0</sup> and

**Table 2**

Percentage of the surface atomic concentration as a function of time for the Cu-sputtered cotton samples as determined by XPS.

Sputtering time (s)	O	Cu	C	N
0	28.9	0	70.2	0.8
20	20.9	11.9	65.6	1.52
40	30.7	21.3	46.8	1.1
90	26.3	29.6	42.3	1.7
180	26.3	29.7	44	0



**Table 3**  
Bacterial inactivation times as a function of sputtering time and film Cu-content.

Sample sputtering time	0 s		20 s		40 s		180 s	
Cu-concentration w/w	0		0.042%		0.060%		0.294%	
Inactivation time (min) of <i>E. coli</i>	Dark	Light	Dark	Light	Dark	Light	Dark	Light
	N.R.	N.R.	N.R.	N.R.	120	30	120	30

N.R.: not reached.

Cu<sup>1+</sup> component at 933.1 eV could not be unambiguously deconvoluted without introducing a large approximation when assigning separately the peaks for Cu<sup>0</sup> and Cu<sup>1+</sup> [19,20]. The Cu<sup>2+</sup> peak is noted in Fig. 6 at 934.2 eV and the small Cu<sup>3+</sup> peak at the right hand side at 937.1 eV has been assigned according to Teterin [25] and Bianconi [26]. The various redox potentials available at the Cu-surface are due to the different oxidation states for Cu. In effect, Table 1 shows by XPS measurements that cotton samples sputtered for 40 and 180 s present various Cu-oxidation states at different depths. More important, the amount of Cu for the 40 s sample is 0.060% w/w and for the 180 s sample is 0.294% w/w as said before but the bacterial inactivation kinetics occurs within the same times in the dark and under light for both samples. Therefore, Cu<sup>0</sup> is not the main active responsible for the *E. coli* inactivation but the ionic species seem to be the species leading to bacterial deactivation as described in Table 1. Table 3 shows the inactivation times as a function of sputtering time and film Cu-content.

The bacterial inactivation of *E. coli* may be due to: (a) surface cotton Cu-clusters and (b) protected Cu-clusters inside the cotton fabric. The topmost surface Cu-layers in the open structure of the cotton fabric would protect the interior lying Cu-layers with ionic species interacting with *E. coli*. This provides additional stability for the internal Cu-clusters during the *E. coli* inactivation process. The overall charge of the *E. coli* is negative between pH 3 and 9, due to the predominant carboxylic external groups of the bacterial cell wall. These carboxylic and other negative functional groups upon dissociation in aqueous solution make the cell wall negative. The opposite charge on the bacteria and the Cu positive-ions as shown in Table 1 seem to induce to a tight binding of the Cu-clusters to the bacterial surface.

No time dependent XPS analysis of the surface atomic concentration as shown in Table 2 could be carried out during and after

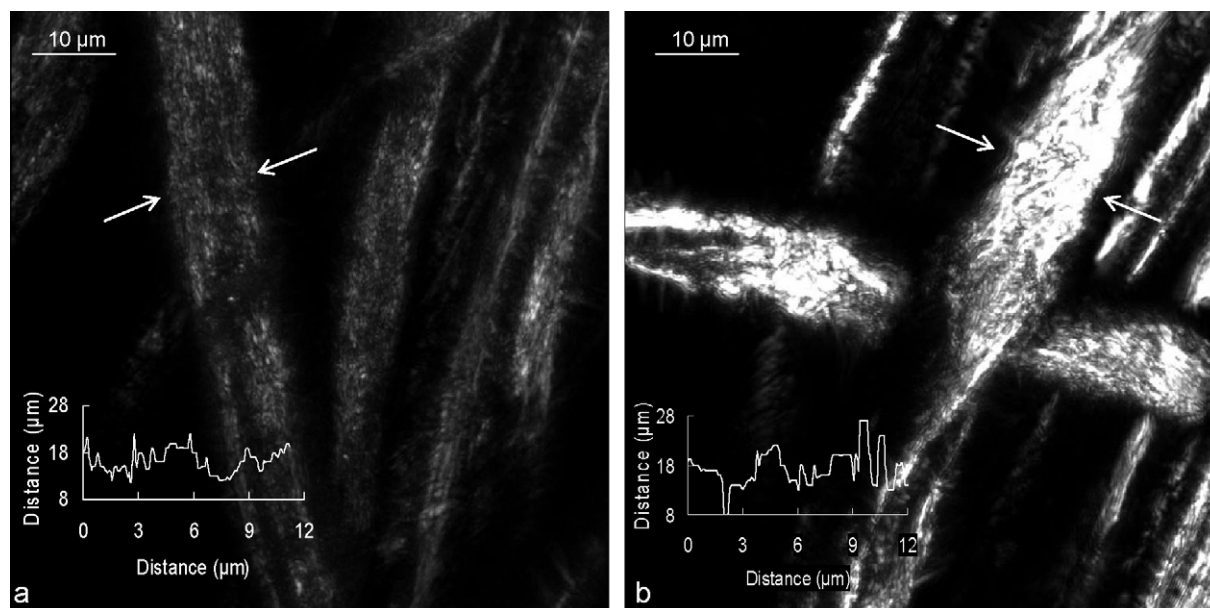
the bacterial inactivation on the Cu-cotton samples. The samples get contaminated during the reactions necessary for the evaluation of the *E. coli* inactivation (see Section 2.3).

### 3.6. Confocal microscopy of cotton and Cu-cotton samples

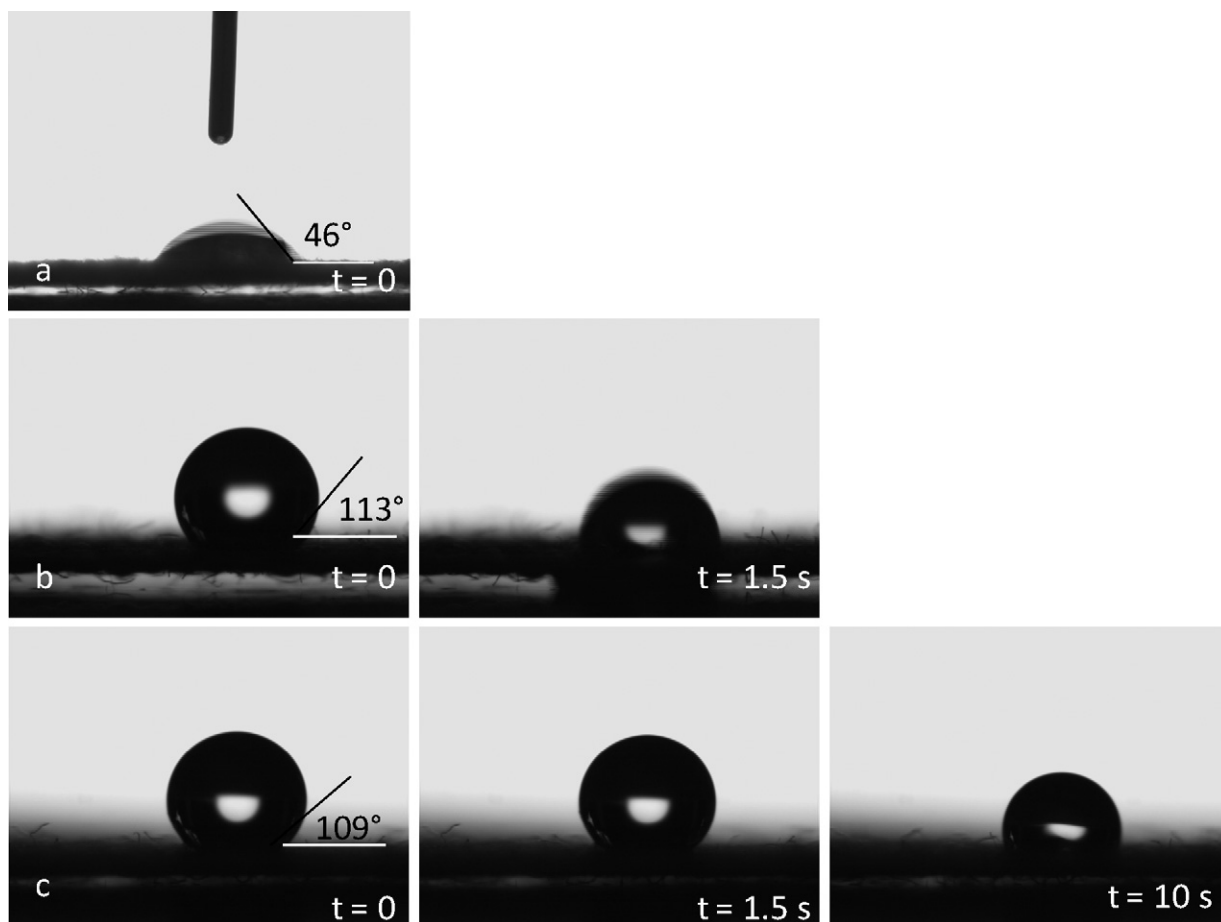
Fig. 7 shows the confocal microscopy of cotton and Cu-sputtered cotton. This technique has been selected since the topography and surface profile being very rough cannot be investigated by AFM in the micron range. The information sought by confocal microscopy enables us to obtain additional information for the structure of the Cu-cotton fabrics beyond the description reported by HRTEM in Fig. 5. The cross-sections in Fig. 7a and b reveal a rougher surface for the Cu-sputtered fiber respect to the bare cotton fiber. The Cu-nanoparticles get attached to the cotton fiber surface and also penetrate inside the cotton fiber. The dark and clear zones in Fig. 7a and b refer to the density of the valleys and peaks for the cotton and Cu-cotton samples. The insets in Fig. 7a and b show that the valleys and peaks for the cotton between the arrows are different for the Cu-cotton sample with respect to cotton alone.

### 3.7. Contact angle measurements and droplet adsorption times

Fig. 8 presents the results of the contact angle measurements. Cotton is hydrophilic by nature. The decrease or increase of the hydrophilicity of textiles is a function of the nature of the textile surface and can be modified according to the ulterior use of the textile. Fig. 8a, shows a contact angle of 46° for bare cotton revealing a hydrophilic surface. For Cu-cotton samples sputtered for 40 s – the threshold of bacterial *E. coli* inactivation – the contact angle shows an increase to 113° in Fig. 8b, well in the range



**Fig. 7.** Reflection confocal microscopy of: (a) cotton and (b) Cu DC-magnetron sputtered cotton. The valleys in the insets correspond to the dark areas and the peaks to the clear areas. In Fig. 8b the reflection of the Cu in the confocal microscopy can be seen.



**Fig. 8.** Water droplet contact angle as a function of the droplet residence time on Cu-cotton samples: (a) cotton alone, (b) sputtered for 40 s and (c) sputtered for 90 s.

of hydrophobic surfaces. The water droplet is seen in Fig. 8b at 1.5 s to rapidly adsorb on the cotton. The increase in hydrophobicity is readily seen for Cu-sputtered samples for 90 s in Fig. 8c. Although the contact angle remained similar to the one observed in Fig. 8b, the adsorption of the water droplet slows down compared to Fig. 8b. Water easily penetrates the untreated cotton (Fig. 8a) and the Cu-clusters sputtered on cotton attain a depth 8 nm or more (see Table 1) reducing the hydrophilic area of the cotton surfaces. Concomitantly, the void area inside the cotton fabrics is reduced during the sputtering process further decreasing water penetration. Hence, the Cu-deposition enhances the hydrophobicity of cotton fabrics.

#### 4. Conclusions

- This is a study addressing the DC-magnetron sputtering Cu-cotton mediated *E. coli* bacterial inactivation. Quantitative information about the Cu-cotton structure and the bacterial inactivation kinetics in the dark and under light is described.
- Low intensity visible light accelerates the bacterial inactivation compared to Cu-cotton inactivation in the dark. Visible light induced charge separation seems to take place and is possible since the red light absorption edge of CuO is 720 nm.
- This suggests that the 40 s sputtered sample allows the highest amount of Cu-sites held in exposed surface positions in the cotton to interact with *E. coli*. The sputtering for 40 s produces the optimal balance of film thickness, crystallite size and roughness therefore exposing maximum surface area to the bacterial sample.

#### Acknowledgments

We wish to thank the COST Action MP0804 Highly Ionized Pulse Plasma Processes (HIPP) for the support of this work. C. Castro thanks Colciencias, the EPFL seed money: Argentinean Swiss Cooperation in nanomaterials for bacterial inactivation and SENA for financial support.

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