Magnetron-Sputtered Ag Surfaces. New Evidence for the Nature of the Ag Ions Intervening in Bacterial Inactivation

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ABSTRACT DC-magnetron sputtering with an Ag target on textile surfaces produced Ag particles with sizes ~4.7 nm (±15%). Sputtering for 15 s led to Ag layers of 15−20 nm. The threshold sputtering time precluding airborne bacterial growth was about 60 s. In this case, the coating was ~40−50 nm thick and the cotton Ag loading was 0.0026 wt %. The Ag particle size did not vary significantly with sputtering time between 15 and 600 s. Only coatings above this thickness lead to bacterial inactivation. Ag/Pt targets with sputtering times <60 s did not increase the bactericide performance of the Ag cotton samples with respect to sputtering from an Ag target alone, as expected from the position of Pt respect to Ag in the electrochemical series (Galvanic effect). The Ag cotton deposition led to very thin metallic semitransparent gray color coatings. X-ray of the Ag cotton suggested the presence of amorphous and crystalline Ag species. By X-ray photoelectron spectroscopy (XPS), it was found that the amount of oxidized silver species on the cotton was similar for sputtering times of 60 and 600 s, but the total amount of Ag deposited was almost two times higher after 600 s sputtering. This suggests that the positive silver-ions were located mainly at the silver interface. The type of silver ions produced using the Ag/Pt sputtering was determined to be very similar at 15, 60, and 600 s with the silver ions produced with the Ag target. This explains the lack of an increased inhibitory effect of Pt during the inactivation of airborne bacteria when present in the Pt/Ag target with respect to the Ag target, because in both cases similar silver ionic species were found.

KEYWORDS: magnetron sputtering • Ag/target • Ag/Pt target • airborne bacteria • Ag(II) ions • Auger Ag lines.

INTRODUCTION

The interest in using bactericide textiles to treat skin diseases has significantly increased during the last several years. Silver is a disinfectant having a broad bactericide spectrum (1−3). At low concentrations, silver ions are effective against bacteria and fungi in aqueous solution. Bacteria have a low resistance to Ag, yet Ag is known to be benign to human cells (4, 5). The recent progress in the deposition of Ag nanoparticles on textiles is a favorable development since a significant amount of Ag atoms/clusters on the surface of the support is exposed without hindrance to the surrounding medium (4−15).

The Ag deposition on cotton is important because cotton has the property to adsorb a large amount of moisture, making this textile prone to microbial attack. With ambient temperature and humidity, cotton is a nutrient for bacterial and fungal growth. To preclude bacterial growth, we reported the preparation of Ag on wound pads by wet impregnation/reduction of $AgNO_3$ to inactivate airborne bacteria originated infections (6−8). This study aims at the reduction of the amount of Ag necessary to attain bactericide action on the cotton compared to our previous work (6) and to produce Ag coatings having a strong adhesion that would not smearing under friction. Bactericide Ag coatings on several substrates has been reported (9−12). The deposition of Ag films on polyamide, silica, and stainless steel plates has been recently addressed (13−15).

Silver nitrate is commonly used as a bactericide agent (14), but silver nitrate is not desirable for textiles, as it stains the textiles black-brown because of the reduction of silver nitrate leading showing low adhesion of the silver to the cotton (6−8). The Ag^o particles and Ag^{1+} and Ag^{2+} ions are produced by the Ag and Ag/Pt-targets with high energies in the sputtering chamber (15−21). These Ag-ions ions existing first in the gas phase are later deposited along Ag^o on the cotton surface. Ag-ions have been reported to be responsible for the elimination of vital elements in the bacterial metabolism as Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions leading to bacterial inactivation (1−10, 21).

Supported Ag clusters prepared by magnetron sputtering seems a promising approach to fix the Ag nanoparticles and
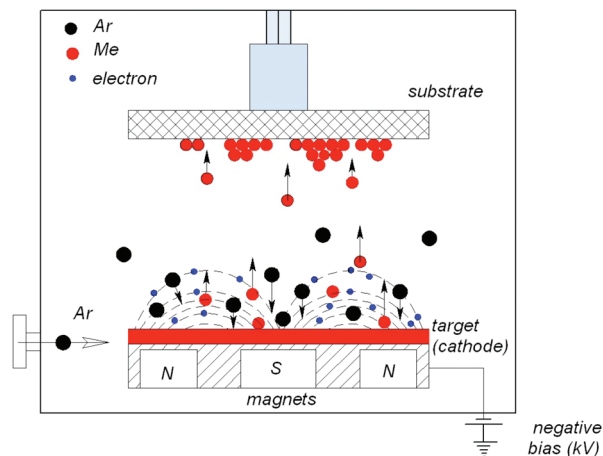
FIGURE 1. Schematic diagram of the DC-magnetron sputtering. Me stands for the metal used as the target and N and S stand for the poles in the magnetron unit.

has been tried on substrates like SiO_2 (16, 17), polypropylene nonwoven fabrics (18), polylactic medical dressings (19), and on artificial fibers wound pads (20). But magnetron sputtering of Ag has not been reported on cotton fabrics for airborne bacteria and the Ag ionic surface species have not been unambiguously identified. The aim of this study is to produce cotton/Ag composites by magnetron sputtering showing: (a) an acceptable bactericide activity; (b) a strong Ag adhesion to cotton during long-term operation; (c) small clusters of Ag having a high surface to volume ratio. This is important because Ag nanoparticle bactericide activity is a function of the particle dimension. The smaller the Ag particle, the more effective the bacterial inactivation (21); (d) a low threshold for Ag (also called minimum inhibitory concentration (MIC) effective in the bactericide action; and finally, (e) a thin enough Ag coating that would not modify the textile handling (semitransparent Ag layers).

The coating of Ag on cotton will be characterized by X-ray-fluorescence, X-ray diffraction (XRD), electron microscopy (TEM and HRTEM), diffuse reflection spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL SECTION

Ag Deposition on Cotton Textiles. Figure 1 shows the schematic diagram of the DC magnetron sputtering. By using magnets behind the cathode to trap free electrons in the magnetic field, the probability of ionizing neutral gas atoms or molecules is enhanced by several orders of magnitude. The positive-ions near the target are accelerated toward the target surface by applying high negative voltages (0.2−2.0 kV): The 5 cm diameter Ag disk is eroded by the impinging energetic ions via energy transfer and the ejected Ag atoms/clusters or ions are collected on the cotton textile. An alloy of 1 % Pt dispersed in Ag was employed to deposit the Ag/Pt on the cotton. The plasma working pressure was in the range of 0.1−1 Pa, the distance between the Ag target and the cotton was about 10 cm and the deposition current was 30 mA. The adhesion of Ag to the cotton was so strong that friction with paper or cloth did not allow smearing of the Ag. This is an improvement respect to the adhesion of Ag particle fixed on activated textiles by reduction of colloidal Ag salts as reported recently (6, 7). Deposition times of 3, 7, 15, 30, 60, and 600 s lead to Ag and Ag/Pt layers of 4.65, 10.85, 23.3, 46.5, 93, and 930 nm
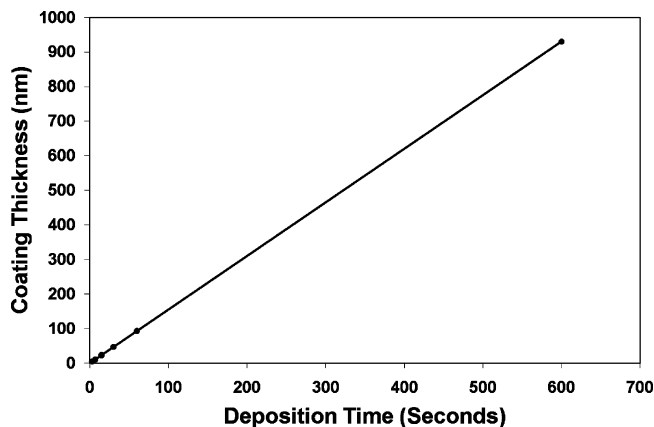

FIGURE 2. Ag thickness layer vs deposition time obtained on glass slides by magnetron sputtering.

thickness on the cotton surface. This is shown in Figure 2. The coating deposition rates were obtained using glass slide samples mounted on the substrate holder. The coating thickness was measured using a Tencor Alphastep profilometer.

X-ray Fluorescence Determination of Ag and Ag/Pt Content on the Cotton Surface. The Ag and the Pt content of the cotton were 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.

High-Resolution Transmission Electron Microscopy (HR-TEM). 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 Ag clusters. The textiles were embedded in epoxy resin (Embed 812) and the fabrics were cross-sectioned with an ultramicrotome (Ultracut E) to a thin section of 50−70 nm. Magnification from about 6800× to 41 000× was used to identify the Ag clusters and determinate the Ag layer thickness.

Airborne Bacterial/Fungi Determination on the Ag Cotton. The inactivation of bacteria and fungi of the cotton-Ag were evaluated in Petri dishes exposing the 1 cm^2 cotton samples to air at room atmosphere for 2 h. The samples were then placed on an agar (Plate Count Agar, ref 1.05463.0500 Merck) in a Petri dish ca. 9 cm in diameter and incubated in the absence of air for 24 h at 34 °C (±2 °C) (17, 21). The cotton samples were surrounded by a dark bacteria/fungi deposit, whereas the cotton samples with Ag did not show any bacterial growth after the incubation period. Each determination was carried out in triplicate.

Diffuse Reflectance Spectroscopy (DRS). Diffuse reflectance spectra were measured using a Cary 5 UV−vis-NIR spectrophotometer equipped with an integration sphere. Measurements were carried out on 2.5 × 2.5 cm^2 size samples.

X-ray Diffraction (XRD). The Ag loaded on the cotton was explored with the help of a Siemens X-ray diffractometer using Cu Kα radiation.

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 elemental compositions were determined from peak areas using experimentally determined sensitivity factors and spec-

APPLIED MATERIALS &INTERFACES

Table 1. Ag and Pt Content of the Cotton Samples at Different Sputtering Times Determined by X-ray Fluorescence

| sample	Ag wt %	Pt wt %
Ag-cotton 3s	<0.001	<0.001
Ag-cotton 15 s	0.0015	<0.001
Ag-cotton 60 s	0.0026	<0.001
Ag-cotton 600 s	0.0385	<0.001
Ag/Pt-cotton 3 s	<0.001	<0.001
Ag/Pt-cotton 15 s	0.0010	<0.001
Ag/Pt-cotton 30 s	0.0034	0.0014
Ag/Pt-cotton 60 s	0.0540	0.0073
Ag/Pt-cotton 600 s	0.0630	0.0078
cotton reference	<0.001	<0.001

(a)   (b)
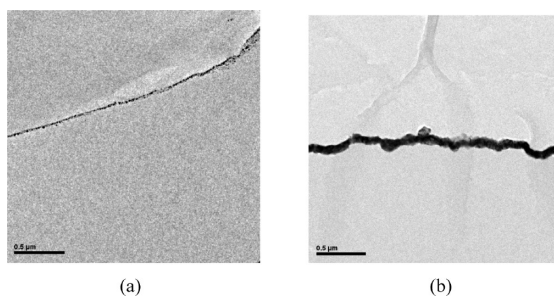
FIGURE 3. TEM images of (a) Ag-cotton with 15 s deposition and (b) Ag-cotton with 600 s deposition (6800×).

trometer transmission function (23, 24). Spectrum background was subtracted according to Shirley (22). The high-resolution spectra were analyzed by means of spectra deconvolution software (Vision 2, Kratos Analytical UK). In the XPS spectra, the Auger lines are a side effect of the XPS method.

RESULTS AND DISCUSSION

X-ray Fluorescence of Ag and Ag/Pt Sputtered Cotton Textile Samples. Table 1 shows the Ag and Pt content determined by X-ray fluorescence at different sputtering times. For the samples sputtered with Ag only, it is seen in Table 1 that the amount of Ag increases on the cotton from 3 s up to 600 s sputtering time. When an Ag/Pt target was employed, the amount of Ag increases attaining a higher Ag amount up to 600 s compared with the Ag target. The implications of these results will be discussed below in the XPS section when describing the results of the inactivation of airborne bacteria on the Ag and Ag/Pt samples.

High-Resolution Transmission Electron Microscopy (HRTEM) of Ag Cotton and Ag/Pt Cotton Fabrics. Transmission electron microscopy of Ag-cotton fabrics with 15 and 600 s deposition are shown in images a and b in Figure 3, respectively, showing the formation of a continuous Ag layer(s) on the cotton surface. The average Ag particle size was found to be ∼4.7 nm (±15%) for samples sputtered 15 s, as shown in Figure 4. In Figure 3a, Ag layers of 15−20 nm were found on the cotton when sputtered for 15 s (3−4 Ag layers), and in Figure 3b a coating of 80−100 nm (20−25 Ag layers) were found for samples sputtered for 600 s. Not much difference was found for the Ag cluster size when the sputtering time was increased from 15 s up to 600 s. Similar layer thicknesses to the previously
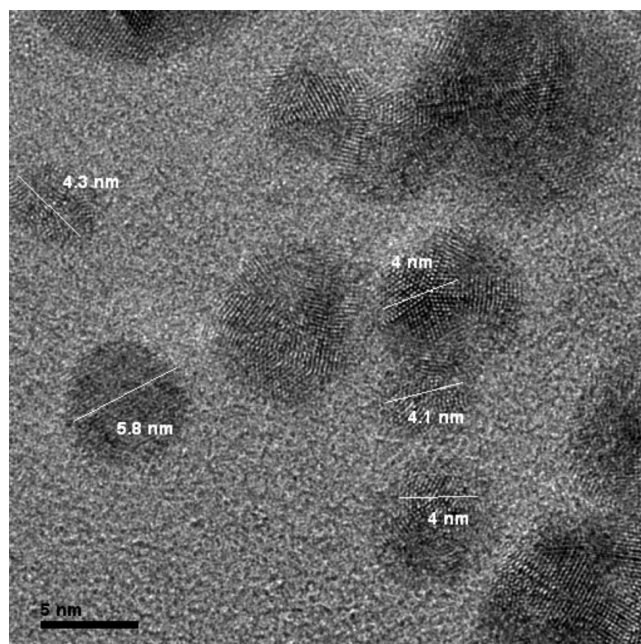
FIGURE 4. HRTEM of Ag-cotton showing the Ag clusters (scale of 5 nm).

mentioned were found when the Ag/Pt target was used. Also, the basic Ag/Pt cluster particle size was similar to the one found when the Ag-target was used. This is interesting because Table 1 shows that at longer sputtering times more Ag is deposited when the Ag/Pt target was used compared to the Ag target. The small Ag and Ag/Pt particle sizes lead to semitransparent films. This feature is important when colored bactericide textiles are prepared, because it is desired to conserve the original color of the fabric for specific applications. Figure 5 shows the energy-dispersive X-ray (EDX) of the Ag/Pt cotton sample sputtered for 600 s. In Figure 5, (a) the peaks for the Ag deposited on the cotton, (b) the small peaks of the Pt, since the target used contained only 1 % Pt, and (c) the Cu signals due to the Cu grid-support used for the Ag/Pt sample are readily seen. No atomic force microscopy (AFM) could be carried out on these samples because of the rough cotton surface.

Inactivation of Airborne Bacteria. Ag-cotton samples sputtered with times <60 s showed no bactericide action. The appearance of punctual deposits around the borders of the 1 × 1 cm cotton samples was indicative of bacterial growth. This is shown in Figure 6a. We investigated the nature of the airborne bacteria and detected E. coli K12 and many other bacterial strands. Because we could not identify the nature of all the airborne bacterial strands, we decided to perform the experiments to see whether the Ag-cotton was able to suppress the airborne bacteria irrespective of their detailed nature comparing cotton samples with Ag-cotton samples. The results are reported in Figure 6.

Figure 6b shows that for Ag-cotton sputtered for 60 s or longer times up to 600 s, the bacterial deposits do not appear on the cotton or around the cotton borders (Figure 6b). About 60 s sputtering time was necessary to deposit 0.0026 wt % Ag on the cotton, as shown in Table 1. This is the minimum amount of Ag necessary to inhibit bacterial/fungal
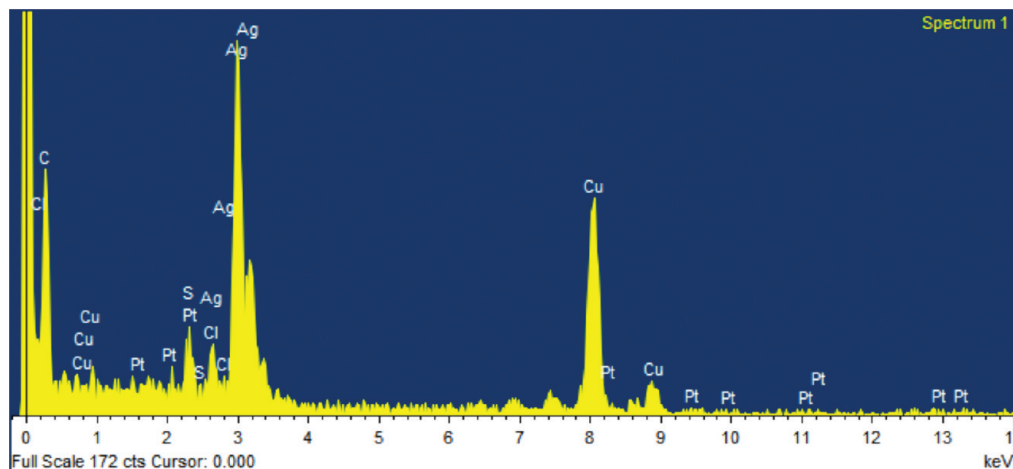
FIGURE 5. Energy-dispersive X-ray (EDX) of the cotton-Ag/Pt sample sputtered for 600 s.
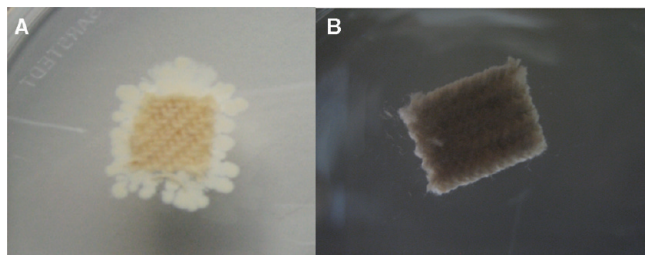

FIGURE 6. (a) Nonsputtered cotton sample showing the growth of airborne bacteria after the incubation period. (b) Ag-sputtered cotton sample. The clear boundaries are due to the original color of the cotton fabric. No bacteria or fungi growth was observed.
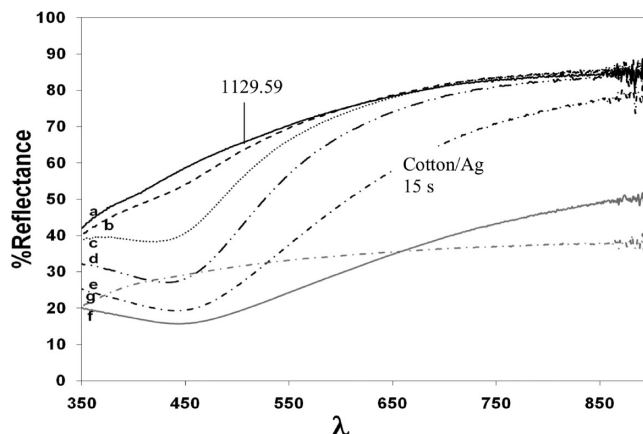

FIGURE 7. Diffuse reflectance spectra of (a) cotton fabric, (b) Ag-cotton with 3 s deposition, (c) Ag-cotton with 7 s deposition, (d) Ag-cotton with 15 s deposition, (e) Ag-cotton with 30 s deposition, (f) Ag-cotton with 60 s deposition, (g) Ag-cotton with 600 s deposition.

after the incubation period described in the Experimental Section. This Ag threshold is equivalent to ∼10 Ag layers (40−50 nm) and is the called the minimal inhibitory concentration (MIC) (17−20). Only an Ag thickness above this threshold induced bactericide properties on the cotton. The amount of Ag necessary to achieve bactericide cotton needed 60s sputtering time and it is short making an economic use of Ag. The Ag ions on the surface of Ag coatings have been reported to increase with increasing Ag layer thickness on several substrates (1−7, 9−11).

Diffuse Reflectance Spectroscopy (DRS) of Ag-Cotton Samples. The DRS spectra of Ag-coated cotton and Ag/Pt-cotton are showed in Figure 7. After 3 s of Ag deposition (Figure 7, trace b), the DRS spectrum is similar to pure cotton (Figure 7, trace a) but shows a small absorption at 450 nm associated with Ag. A sharp decrease in reflectance is observed when the sputtering time was increased up to 60 s (Figure 7, traces c−e). A heavy silver gray layer is observed for the sample sputtered for 600 s (Figure 7, trace f). The Ag/Pt-cotton samples showed a similar DRS pattern to the Ag-cotton samples, but no absorption peak associated with Pt was observed. Only a slight decrease on absorption spectra was due to the presence of platinum (26).

X-ray Diffraction of Ag-Cotton Textile Samples (XRD). The X-ray diffraction of the sample Ag-cotton 600 s showed a weak peak around 38° attributed to Ag. Ag-cotton samples sputtered with shorter times did not have enough Ag-loading to be detected by the instrument used. The Ag is amorphous or poorly crystallized, but the signal was too weak to be detectable unambiguously identified. The Ag peak was not found on the pure cotton sample.

XPS Analysis of Cotton Samples Loaded with Ag and Ag/Pt by Magnetron Sputtering in Vacuum after 15, 60, and 600 s. XPS analysis of cotton samples loaded with Ag and Ag/Pt by magnetron sputtering in vacuum after 15, 60, and 600 s. XPS analysis of pure cotton gives a surface atomic concentration/composition: 82.7 % of C 15.8 % of O, 1.10 % of N, and 0.43 % of Ca (Table 2). Samples of cotton loaded with Ag at 15, 60, and 600 s present a surface atomic concentration of 7.31, 23.36, and 37.76 % of Ag, respectively (Table 2). These data have been taken for 3 different samples and the experimental error

Table 2. Surface Atomic Concentration in % of Cotton Loaded with Ag and Ag/Pt

sample	O	Ag	C	N	Ca	Cl	S	Pt
cotton ref	15.80		82.67	1.10	0.43			
cotton +Ag $t = 15$ s	11.90	7.31	79.18			0.29	0.51	0.81
cotton +Ag $t = 60$ s	6.33	23.36	69.63				0.68	
cotton +Ag $t = 600$ s	5.92	37.76	56.33					
cotton + Ag/ Pt $t = 15$ s	11.91	9.41	77.65			0.33	0.58	0.12
cotton +Ag/Pt $t = 60$ s	8.90	18.49	71.46				0.89	0.25
cotton +Ag/Pt $t = 600$ s	7.25	35.28	57.15					0.32

Table 3. Auger Parameters for Ag Deposited on Cotton Samples

sputtering time	cotton/Ag Auger parameter, α	cotton/Ag/Pt Auger parameter, α
15 s	725.15	725.53
60 s	725.66	725.53
600 s	725.65	725.66

reported in Table 2 was 10−15 %. Increasing the sputtering time increases the amount of Ag in the topmost layers with concomitant decrease of the O and C as shown in Table 2. For most elements, the exact position of the XPS peak is related to the oxidation state of the element. But for some elements as Ag, the situation is more complex because of specific ionization/relaxation phenomena (22). The chemical shift rules do not work in the usual way. Therefore, we used XPS and Auger lines to follow the changes in the oxidation state of Ag (24). We introduced in Table 3 the "Auger parameter" α to follow the Ag-oxidation state taking into account the difference between the chemical states from Ag^0 to Ag^{2+}. This parameter is defined as $\alpha = Ag_3d_{5/2}(BE) + Ag\ M_4N_{45}N_{45}$ (KE). The $Ag_3d_{5/2}$ (BE) is related to the XPS line and Ag $M_4N_{45}N_{45}$ (KE) to the Auger line. The α-value is independent of the static charging and of the work function. It is more accurate than the simple core level BE or Auger peak value in KE. The α values for the Ag-cotton samples are shown in Table 3 and Figure 8, respectively. Figure 8 shows Auger lines of the Ag-cotton samples. The line at around 1129 eV binding energy equal to 357.6 eV kinetic energy
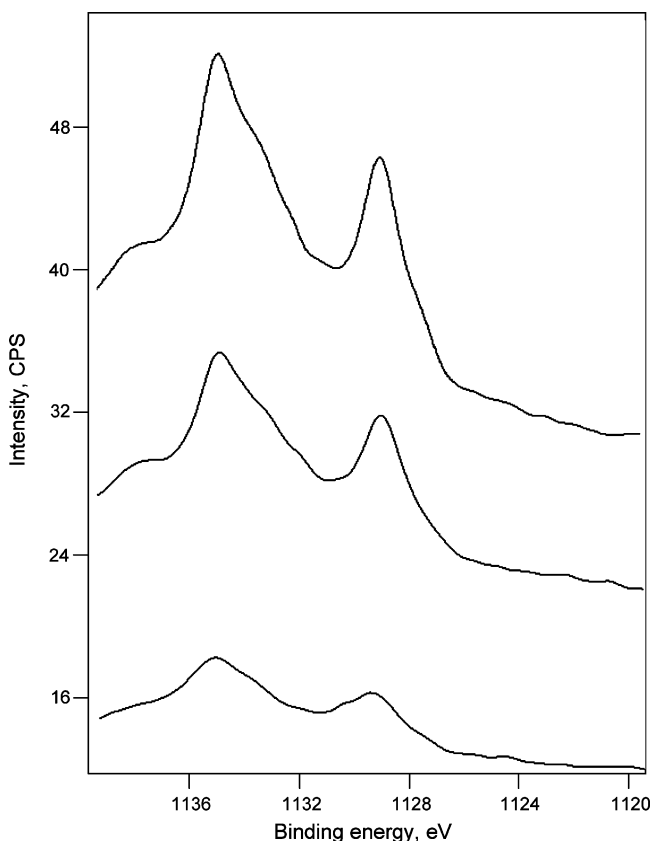
FIGURE 8. Auger Ag lines for Ag-cotton samples sputtered at different times.
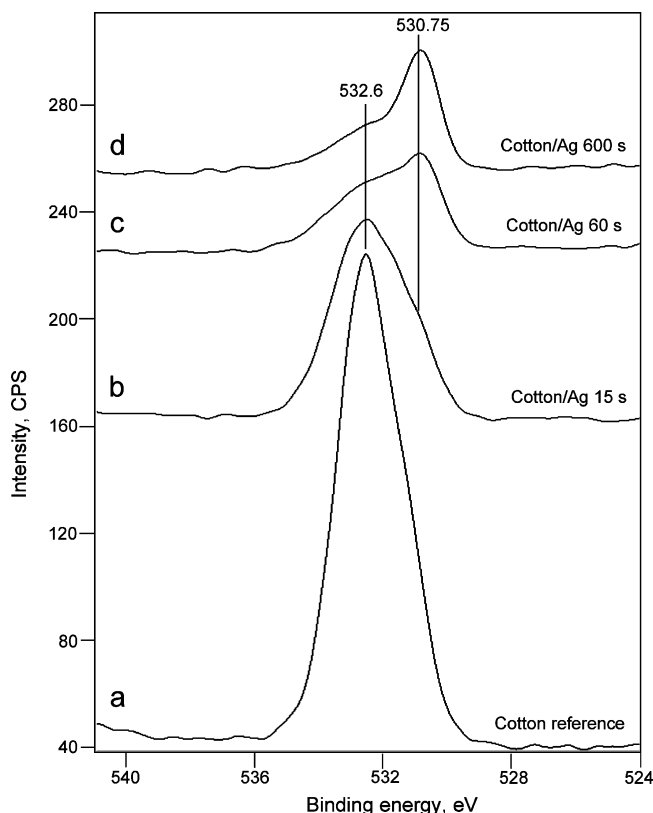
FIGURE 9. XPS O1s line of cotton and for Ag-cotton samples at different sputtering times.

was used to calculate the value of Auger parameter α. For reference purposes a multicomponent line at 1135 eV binding energy (351.6 eV kinetic energy) is the Auger line Ag $M_5N_{45}N_{45}$. Table 3 shows that the highest Ag-oxidation state was found after the shortest deposition time (15 s). In this case, the Auger parameter was 725.15 eV and the Ag-content for the cotton sample was low (see Table 2). At longer deposition times, a significant shift of Auger parameter from 725.15 to 725.65 eV in Table 3 indicates a higher deposition of AgO.

The observation of Ag(II)O on the cotton is based on the evolution of the O1s line in Figure 9. A detailed analysis of the oxygen O1s line shows that Ag coats cotton homogeneously. Because of this, the cotton signal at 532.6 eV drastically decreases (Figure 9a−c) giving rise to a new component for the O1s line at 530.75 eV (Figure 9c,d). This is oxygen bonded to Ag and its position suggests the presence of Ag(II)O as the major Ag-oxidized species for both 60s and 600s samples (22−24). The amount of oxidized silver was observed to be similar for samples sputtered during 60 and 600 s (Figure 9c,d) while at the same time the total amount of Ag was almost two times higher after 600 s sputtering (Figure 8b,c). This indicates that the positive Ag ions are located mainly at the silver interface.

Samples of cotton loaded with Ag/Pt at 15, 60 and 600s present an atomic surface concentration of 9.41, 18.46, and 35.28 % along 0.12, 0.25 and 0.32 % of Pt (Table 2). Three types of silver could be suggested in Table 3, with Auger parameters 725.15, 725.53, and 725.66 assigned to the presence of Ag^0, Ag^{1+} and Ag^{2+}, in this order. Although the

Table 4. Platinum Contents in Two Forms on Cotton Loaded with Ag/Pt

sample	Pt^0 %	PtO %
15 s	32.2	67.8
60 s	48.7	51.1
600 s	87.55	12.45

presence of Ag^0 and Ag^{2+} seems to be documented, the assignment to Ag^{1+} is less clear. The reason for that is that O1s line at 530.71 eV results from the presence of two Ag and Pt oxides and for this reason cannot be used for clear identification of the Ag oxidation state.

In the samples loaded with Ag/Pt, the Pt peak shows three components, which are a combination of two doublets of two different Pt 4f lines. Each doublet has two components, Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$, and they are 3.35 eV apart. Two types of platinum were determined: (i) Pt^0 with a Pt 4f$_{7/2}$ component at 70.41 eV and (ii) platinum Pt^{2+} with a Pt 4f$_{7/2}$ component at 73.27 eV. The contents of Pt^0 and PtO calculated from the decomposition of the Pt 4f peak are presented in Table 4. Silver XPS lines for the different oxidation states are well-known for their poor chemical shift sensitivity <0.2 eV. Therefore, it is possible only to qualitatively estimate the different oxidation states of Ag. For a quantitative evaluation, we need to know the exact position of each Ag component with a precision of >0.01 eV, which is not possible.

The striking observation is that the type of Ag ions produced by the Ag/Pt target is similar to that of the Ag target for the three sputtering times of 15, 60, and 600 s (Table 3). This explains the lack of an increased inhibitory effect of the Pt in the Pt/Ag target with respect to the Ag target to inactivate. In both cases, similar Ag ionic species were produced. The Ag/Pt did not shorten the sputtering times below 60 s, the time necessary to prepare cotton with bactericide properties indicating that Pt did not enhance the release of Ag ions from the Ag/Pt target, as expected from the position of Pt in the electrochemical series respect to Ag (25). The Pt is positioned higher in the galvanic scale respect than Ag and should therefore enhance the formation of Ag ion through a galvanic effect. This was not observed by XPS spectroscopy when comparing both targets. The lack of solubility of Pt in the Ag network may be one of the causes for this. In principle, substitution of Pt in the Ag network is possible because of the close atomic radii of 1.26.

CONCLUSIONS

• Sputtering from an Ag target for 60 s produced thin semitransparent coatings with 4−5 layers showing strong adherence and bactericide activity and did not affect the handle or touch of the cotton textile.

• The amount of Ag necessary to achieve bactericide cotton sputtering only for 60 s is short. This shows that Ag sputtering on cotton makes an economic use of Ag.

• An increase in the Ag ions release with Ag/Pt target with sputtering times <60 s did not take place compared with the release from an Ag target. This is expected from the position of Pt in the electrochemical series with respect to Ag.

• Sputtering at times between 60 and 600 s produced inactivation of airborne bacteria using the Pt in the Pt/Ag targets. In both cases, similar Ag ionic species were produced as observed by XPS Auger spectroscopy.

REFERENCES AND NOTES

(1) Zhao, G.; Stevens, E. *Biometals* **1998**, *11*, 27–34.
(2) Fun-Ren, F.; Bard, A. *J. Phys. Chem. B* **2002**, *106*, 279–286.
(3) Demling, R.; de Santi, L. *Wounds* **2001**, *13*, 11–16.
(4) Feng, Q.; Wu, J.; Chen, F.; Kim, J. *Biomed. Mater. Res.* **2000**, *79*, 1118–1124.
(5) Kubacka, A.; Ferrer, M.; Arias, M.; Fernandez-Garcia, M. *Appl. Catal., B* **2008**, *84*, 87–93.
(6) Yuranova, T.; Rincon, A.; Bozzi, A.; Parra, S.; Pulgarin, C.; Albers, P.; Kiwi, J. *J. Photochem. Photobiol., A* **2003**, *16*, 27–34.
(7) Yuranova, T.; Rincon, A.; Pulgarin, C.; Laub, D.; Xanthopoulos, N.; Mathieu, J.-H.; Kiwi, J. *J. Photochem. Photobiol., A* **2006**, *181*, 363–369.
(8) Pohle, D.; Damm, C.; Neuhof, J.; Rooesch, A.; Münstedt, H. *Polym. Compos.* **2001**, *15*, 35–364.
(9) Jeon, H.; Yi, S.; Oh, G. *Biomaterials* **2003**, *24*, 4921–4928.
(10) Jeon, H.; Yeo, Y.; Yi, C. *J. Mater. Sci.* **2005**, *40*, 5407–5411.
(11) Lian, S.; Read, D.; Pugh, J.; Furr, J.; Russel, A. *Lett Appl. Microb.* **1997**, *25*, 279–283.
(12) Radetic, M.; Ilic, V.; Vodnik, V.; Dimitrevic, S.; Jovancic, P.; Saponjic, Z.; Nedeljkovic, M. *Polym Adv. Technol.* **2008**, *19*, 1816–1821.
(13) Gao, Y.; Cranston, R. *Text. Res. J.* **2008**, *78*, 60–72.
(14) Feng, L.; Wu, J.; Chen, Q.; Cui, Z.; Kim, N.; Kim, O. *J. Biomed. Mater. Res.* **2000**, *52*, 662–668.
(15) Bossetti, M.; Masse, A.; Tobin, E.; Cannas, M. *Biomaterials* **2002**, *23*, 887–893.
(16) Morones, R.; Elechiguerra, L.; Camacho, A.; Holt, K.; Kouri, B.; Ramirez, T.; Yacaman, M. *Nanotechnology* **2005**, *16*, 2346–2351.
(17) Scholz, J.; Nocke, G.; Hollstein, F.; Weissbach, A. *Surf. Coat. Technol.* **2005**, *192*, 252–256.
(18) Wang, B.; Wang, Y.; Hong, H.; Gao, W.; Zhu, Z. *J. Coat. Technol. Res.* **2007**, *4*, 101–106.
(19) Wang, H.; Wei, Q.; Wang, X.; Gao, W.; Zhao, X. *Fibers Polym.* **2008**, *9*, 556–560.
(20) Sant, B.; Gill, S.; Burrel, E. *Acta Biomater.* **2007**, *3*, 341–350.
(21) Czajka, R. *Fibers Text. East Eur.* **2005**, *13*, 13–15, and refs therein.
(22) Shirley, D. A. *Phys. Rev. B 5* **1972**, *4709–4716*.
(23) Briggs, D.; Shea, M. In *Practical Surface Analysis*, 2nd ed.; John Wiley & Sons: New York, 1988; Vol. 1, Auger and X-rays.
(24) *Handbook of X-ray Photoelectron spectroscopy*; Wagner, C. D., Riggs, W.M., Davis, L.E., Muilenberg, G.E., Eds.; Perkin-Elmer Corporation Physical Electronics Division: Eden Prairie, MN, 1979.
(25) Dowling, D.; Betts, A.; Pope, C.; McConnell, M.; Eloy, R.; Arnaud, M. *Surf. Coat. Technol.* **2003**, *163*, 637–640.
(26) Huang, H.; Yuan, Q.; Yang, X. *Colloids Surf., B* **2004**, *29*, 31–37.
(27) Lide, D. R. *Handbook of Chemistry and Physics*, 68th ed.; CRC Press, Boca Raton, FL, 1988.

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