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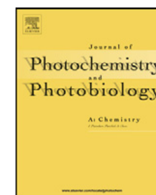

Antimicrobial Cu-functionalized surfaces prepared by bipolar asymmetric DC-pulsed magnetron sputtering (DCP)

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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.

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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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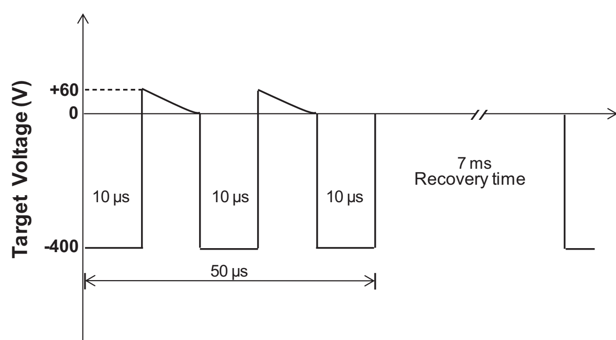

Fig. 1. Asymmetric bipolar DC-magnetron pulse. For other details see text.

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.

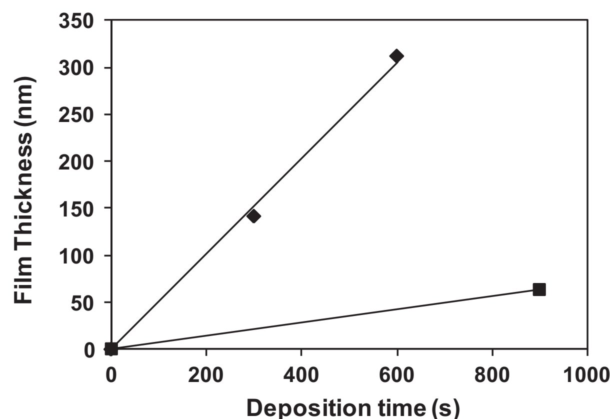

Fig. 2. Cu-layer thickness deposited by PMS as a function of time on Si-wafers. The lower trace corresponds to the thickness of the Cu-layers when using a PMS current of 50 mA and the upper trace corresponds to a PMS current of 300 mA.

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.

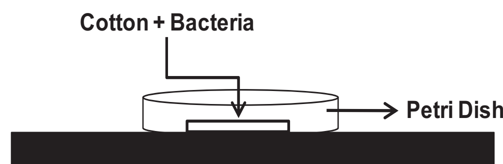

Fig. 3. Scheme of the experimental set-up to monitor the bacterial inactivation.

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