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Application of Cathode Sputtering for Obtaining Ultra-thin Metallic Coatings on Textile Products

Abstract
The need to protect rooms in which people work and sensitive electronic equipment operates against the negative influence of electromagnetic fields (EMF) requires us to search for better and better screening materials, which at the same time would be economically reasonable, and to elaborate more effective manufacturing methods. This paper presents the possibility of using cathode sputtering, a method well-known in micro- and opto-electronics, for manufacturing ultra-thin metallic coatings on textile products, especially nonwovens. The quality and thickness of the deposed metal layers were estimated by scanning electron microscopy (SEM), whereas the attenuation of the coated nonwovens was assessed in accordance to a method described in a US standard, here slightly modified. On the basis of the research carried out, we stated that it is possible to manufacture new screening materials in the shape of wallpapers.

Key words: *electromagnetic fields, screening textiles, metallic coatings, cathode sputtering, electromagnetic wave attenuation.*

Introduction

As the result of the recent enormous increase in the number of electromagnetic field (EMF) sources, such as radio broadcasting, television, radio communication, and mobile phone communication, a necessity has arisen in the public environment to protect banks, municipal & state administration offices and data bases against the disturbing influence of external fields, as well as to diminish the possibility of access to confidential information [1, 2]. Rooms screened with special wallpapers, linings and walls of appropriate construction are the technical means which enable the limitation of the negative effects of EMF.

It is also fundamentally important to screen medical rooms with sensitive electronic apparatus involved in the precise diagnostics and recording of human life-functions during surgical operations. European standards already include conditions for the operation of such apparatus. For example, the standards state that rooms with sensitive medical apparatus should be shielded at a screening level of at least 60 dB, which is related to a 99.9% attenuation of the radiation energy. Such a value cannot be obtained by the use of the majority of conventional screening materials, such as materials manufactured on the basis of carbon. Only metallic and metallised shields, as well as specially designed multilayer systems can achieve the attenuation mentioned above. Metallised textile screening materials have been known since the end of the 1980s. They are mainly obtained by chemical and electrochemical metallisation [3], and are manufactured in many countries, even though that the technological processes used, regarding their production of waste water, are damaging to the environment. In addition, it is not simple to control the layer thickness deposited on the fibres while using these processes.

The aim of our research is to develop a new method of deposing metallic coatings on textile materials, which would be not only effective in screening, but which would principally be obtained by processes which do not generate waste water. Some textile materials manufactured from commonly used polymeric raw materials, such as polypropylene (PP), are very difficult to metallise, considering their surface features. The classical methods of deposing metallic layers do not guarantee that a fast, durable layer will be obtained. The layer deposed is often characterised by very bad adhesion and may be easily abraded. The plasma activation of the materials' surface, followed by the deposition of the metallic layer by vacuum evaporation, is as of now the only known method for metallising polymeric materials. Unfortunately, this is a two-stage process. It is possible to significantly simplify this process, by the method of magnetron (plasma) evaporation, which joins the two processes mentioned above in one. This is a quick, ecological process, practically without yielding any waste, and characterised by high repeatability, stability, and efficiency. The parameters of the deposited layers may be influenced over a broad range. We can obtain very regular layers of the thickness ranging from a few to under twenty nanometres. The magnetron evaporation method is well-known and used mainly in micro- and opto-electronics. This technology is also very interesting from the point of view of its very high efficiency. For example, from one plasma target of 10 mm diameter and 3 mm thickness, a surface area of about 3000 m^2 and 1 μm thickness may be covered. However, this method has not hitherto been used in textile practice. Therefore the main aim of our research was to state whether the method of deposing metallic layers on a textile base, especially on a nonwoven, is possible by magnetron evaporation. The assumed basic difficulty was the selection of process parameters in such a way that the base would not be destroyed by shrinkage, deformation, or even burning. Confirmation of the assumed electrical conductivity of the metallic layers obtained by magnetron evaporation, as well as their ability to screen electromagnetic fields, was just as vital an aim of our research as was developing a method of coating the textile base. A textile product is a three-dimensional object, and the main difficulty of obtaining a high-quality screening material lies in obtaining the best possible continuity of the metallic coating of the fibres in the nonwoven's surface layer, and as many contact points as possible of the individual fibre coatings.

The process of magnetron evaporation may be easily expanded from laboratory scale into industrial conditions. Magnetron plasma guns of different dimensions are commonly available. Also, pump

stands can be chosen and adapted to a standardised production scale. Many well-known enterprises which manufacture vacuum equipment present such offers.

Theoretical basis of cathode sputtering with use of glow discharge

Although vacuum metallisation processes are at present the most commonly applied methods of obtaining thin metallic layers on various bases, they have not hitherto been used for coating textile materials. The basic division of these processes concerns the method of deposing the metal particles by evaporating the metal by the vacuum-thermal method or by cathode sputtering. By the first method, the metal of a resistance tungsten or molybdenum wire, heated by an electric current, is evaporated in a vacuum of 10^{-4} hPa. The vapours obtained condense on the surface of the coated product placed in a vacuum chamber.

The process of cathode sputtering, also called the magnetron evaporation method, differ essentially from the first method by using evaporation and condensation of the elementary particles, even though using a metal electrode and conducting the process in vacuum is common to both methods.

The central principle of cathode sputtering is bombarding an electrode, called the target, by ions of the working gas, whereas the metal ions extracted out from the target's surface are sputtered and deposed on the surface opposite in relation to the electrode. In order to begin 'etching' the metal electrode, it is necessary to initiate a glow discharge of the working gas in an abnormal state – the plasma – in the neighbourhood of the electrode's surface. The plasma includes atoms or neutral non-activated particles, activated atoms, positive and negative ions, electrons and photons. However, in the majority of cases, we can consider the chemical plasma composition in a simplified way as containing only neutral particles, positive ions and electrons [4, 5]. Low-temperature plasma, which is used in the process of etching the electrode, has a temperature below 10^{-4} K. Its source is the incomplete discharge generated by a high-frequency electromagnetic field in a gaseous medium, most often helium, argon and air. After initiating the abnormal glow discharge, a closed plasma ring appears over the electrode. The positive ions of the working gas, for example argon, bombard the material sputtered and cause knock-off of its atoms. The processes of gas ionisation mainly take place during the collisions of neutral gas molecules with the secondary electrons extracted from the electrode. Therefore the gas ionisation in the region near the electrode is higher, which is advantageous for the sputtering speed. With an increase in the power dissipated in the electrode, the ions of the sputtered material appear together with the ions of the working gas. For high power densities, the process of sputtering is maintained autogenously by the ions of the sputtered material. However, the heating of the electrode [6] is a factor which limits the increase in power density, and at the same the sputtering efficiency.

In order to obtain a smooth, regular metallic coat of good quality, it is necessary that during movements in the vacuum chamber from the electrode surface to the sputtered surface, the number of collisions between the metal ions and the air molecules which remain in the vacuum chamber is as small as possible, To fulfil this condition, the average length of the free path of metal ions (without collisions) must be significantly greater than the distance between the surfaces of the electrode and the base. The greater this distance is, and the higher the vacuum, the more regular is the coating obtained (see Figure 1).

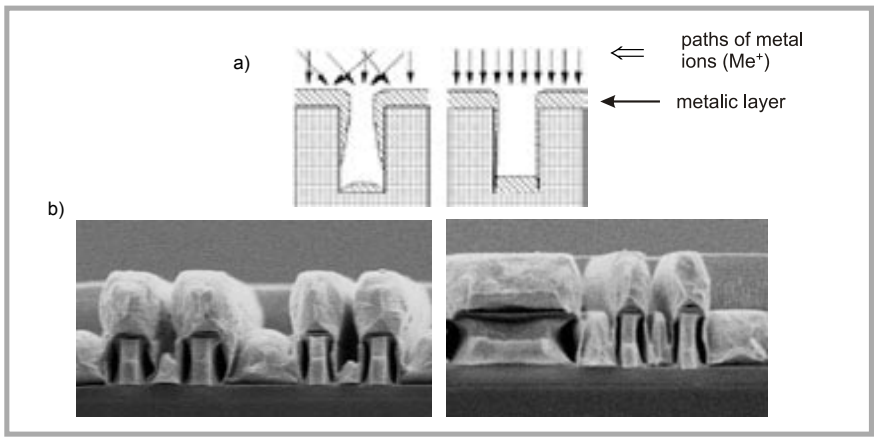

Figure 1. *Depositing a copper layer on a base of differentiated geometry, for various working pressures ($p = 0.39 \times 10^{-3}$ hPa for the left system and $p = 1.3 \times 10^{-3}$ hPa for the right system); a) schematic view, b) SEM photos of the sputtered layer [7].*

Processing method of depositing a copper layer on nonwovens

Device for cathode-sputtering

The process of cathode-sputtering metal layers on selected textile materials was carried out with the use of the WMK-100 circular magnetron gun constructed in the Technical University of Wrocław, Poland. This gun is equipped with a high-voltage electrode system fed from an impulse-supply circuit, and an electrode with a working diameter of 100 mm and a thickness of 7 mm. This system is the basis of the cathode, whereas the anode is a steel casing in the shape of a globe with a height designed according to the electrode dimensions and separated from it by a high-voltage insulator. The casing is fastened to a pressing ring with a maximum 130 mm diameter which seals the vacuum chamber. Four sight-glasses with sockets are fastened on the casing's (anode's) circumference. The WMK-100 magnetron works together with the vacuum system of the rotary- and diffusion pumps. In order to obtain a regular coating of the sputtered metal, the process is conducted in an inert gas atmosphere; we used argon. The precise dosing of the argon was performed by reducing the gas flow with the use of a needle valve with a micrometric screw. Textile materials, in the majority nonwovens, were the objects sputtered in our investigations. Previously prepared disks were freely placed on the pressing ring.

Process of sputtering nonwovens with copper

The process of cathode-sputtering with the magnetron gun was performed every time after establishing the preset vacuum value in the discharging chamber with the disc-sample placed in it. The inner diameter of the chamber was 130 mm, whereas the distance between the elec-

trode and the plate of the sputtering device was 140 mm. The working pressure in the chamber at which the glow discharge of argon began, was 4×10^{-3} hPa, while the argon flow was set at the level of 2 dm^3/min. The time of plasma glowing, and at the same time that of copper sputtering, are parameters which can be set and controlled by appropriate settings of the impulse-supply circuit programmer of the magnetron gun. The end of the process, that is, the break of feeding the magnetron head, is marked by an acoustic signal, and the cessation of the coloured gleam which accompanies the plasma, which can be observed through the magnetron casing's sight glasses.

Handicaps in stabilising the sputtering conditions were short changes, of a period of some seconds, in the pressure value in the discharging chamber, which resulted in an increase in the pressure value up to 2×10^{-2} hPa. The pressure changes usually accompanied the beginning of the argon glow discharging. This is a disadvantageous phenomenon, as it causes an almost immediate temperature increase in the discharging chamber. Unfortunately, this parameter was not recorded. The effect of pressure increase and the increase in the chamber's temperature is an excessive heating of the steel globe, despite the cooling coil fastened to its outer circumference; this can lead to a deformation of the sample caused by shrinkage and a softening of the nonwoven's matter. We suppose that the activation of the gas ionisation process may be the cause of the previously described pressure changes in the chamber. Considering the small globe dimensions of the sputtering device, every change in the state of the gas may be the cause of the gas pressure changes and its temperature. At this stage of our investigation, the process of sputtering the nonwoven base with use of a copper electrode was carried out as a function of two variables: the sputtering time and the intensity of the current which fed the magnetron head. The programme of the planned experiment provided for the use of three nonwoven materials differentiated by the raw material used as the base for copper sputtering. The following nonwovens were used: a spun-bonded polypropylene (PP) nonwoven, and two water-stitched nonwovens, one made of polyester (polyethylene terephtalate – PET) and one of viscose (V) fibres. Nonwovens with various structures resulted from the manufacturing technology, and with possible low area mass, were selected with a view to possible future use as wallpapers.

Discussion of the research results

The samples with a copper coating which we obtained were evaluated by organoleptic and laboratory tests, which enabled us to determine the basic physico-mechanical parameters of the materials processed. Figure 2 presents the views taken by a digital camera of the copper-covered sample surfaces.

Below only those tests which are most important for the subject discussed are described; these are the determination of the surface and through resistances in accordance with the appropriate standards, an analysis of the surface structure of the sputtered layers by electron scanning microscopy (SEM), and tests of the attenuation of electromagnetic radiation in accordance with Standard ASTM D4935-99

Surface and through resistance

The surface and through resistances were determined in accordance with Standard PN-91/P-04871 at a temperature of 23 ± 2 °C, and relative humidity of 50 ± 5 °C. The results are presented in Table 1.

SEM analysis

In order to estimate the structure of the nonwovens tested, microphotographs of their surfaces and cross-sections were taken with the use of a JSM-5200LV(JEOL) scanning electron microscope with magnifications within the range of 50× to 1000×. The nonwoven samples were tested by the low-vacuum technique with the use of a MP-2461 detector of backwards-dispersed electrons. An accelerating voltage of 15 kV and pressure in the sample chamber within the range of 1 to 100 Pa were used. The pictures were recorded by the Semafore System, which enables the user to obtain digital pictures and analyse the picture details' dimensions. The pictures obtained were additionally transformed by the CorelDraw program. Examples of the pictures obtained are presented in the next subsections.

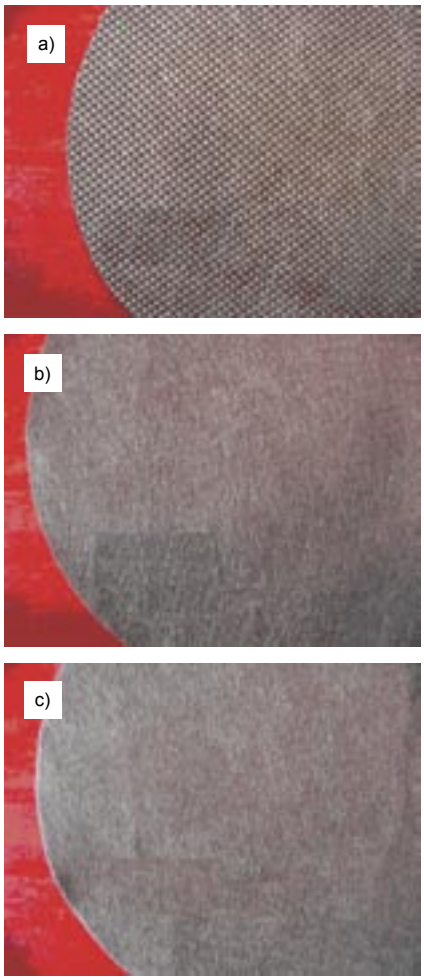

Figure 2. *Views taken by a digital camera of the the copper-covered sample surfaces; a) polypropylene nonwoven (Cu-PP) spun-bonded and spot-welded, b) polyester nonwoven (Cu-PET) stitched by water, c) viscose nonwoven (Cu-V) stitched by water.*

Viscose nonwoven (Cu-V) stitched by water (Figure 3)

As is visible in the cross-section picture, the metal covers only a few fibre layers, on one side, and up to half of their transversal dimension (the bright areas in the pictures). The maximum thickness of the deposited metal layer, measured transversally to the fibre axis, was about

Table 1. *Results of resistance measurements and calculated resistivity of nonwoven samples sputtered with copper.*

Parameter	Cu-PET	Cu-V	Cu-Cu-PP	Test method
surface resistance, Ω	2,8 x 10^8	3,4 x 10^8	2,9 x 10^3	EN-1149-1,2 RH = 50 ± 5% T 23 ± 2 °C
through resistance, Ω	5,6 x 10^9	6,7 x 10^9	5,7 x 10^4	
surface resistivity, Ω	5,4 x 10^7	2,3 x 10^7	4,2 x 10^{12}	
through resistivity, Ωm	2,1 x 10^8	1,0 x 10^8	1,6 x 10^{13}	

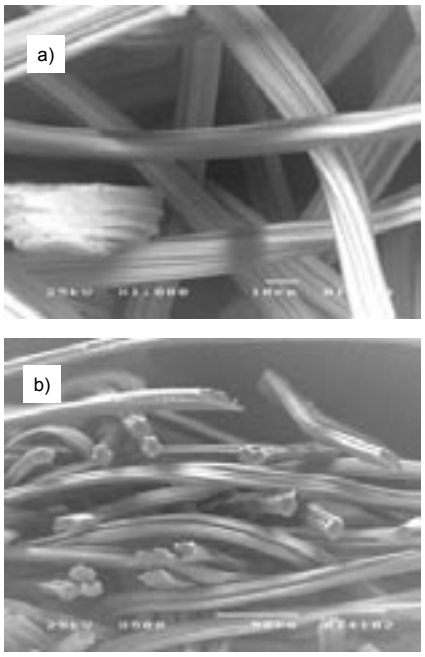

Figure 3. Microscopic photos of a viscose nonwoven (Cu-V) covered by copper; a) view of the fibres from the sputtered surface, b) view of the fibres in the sample's cross-section.

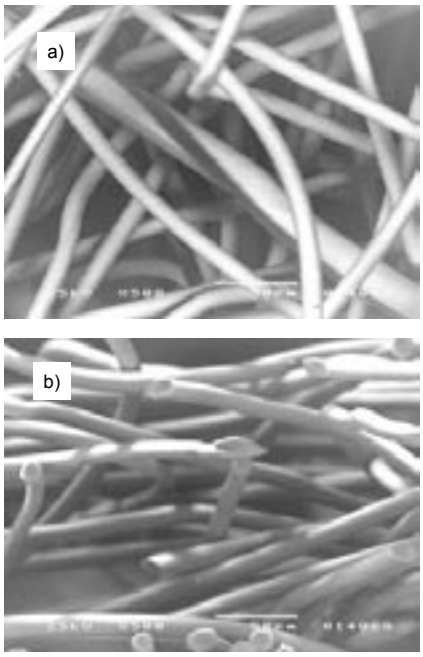

Figure 4. Microscopic photos of a polyester nonwoven (Cu-PET) covered by copper; a) view of the fibres from the sputtered surface, b) view of the fibres in the sample's cross-section.

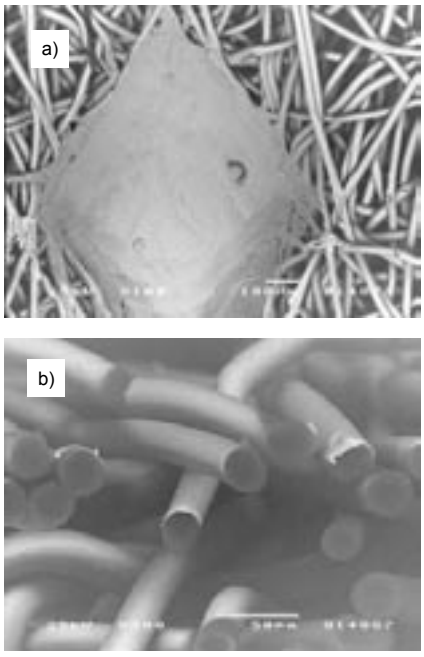

Figure 5. Microscopic photos of a polypropylene nonwoven (Cu-PP) covered by copper; a) view of the fibres from the sputtered surface, b) view of the fibres in the sample's cross-section.

60 nm. The local discontinuities of the electro-conductive layer on the fibres' surfaces, the one-side covering of the fibres, and the possibility of displacing fibres in the nonwoven structure, all visible in the cross-section, may influence the worsening of the conductivity during the products' use .

Polyester nonwoven (Cu-PET) stitched by water (Figure 4)

The fibres are arranged statistically randomly, and are not joined together. On the cross-section picture it is apparent that the metal covers only a few fibre layers, on one side, up to half of their cross-section, and with a thickness which lowers in the direction of the layer's edges. The maximum thickness of the sputtered metal layer was about 100 nm.

Polypropylene (Cu-PP) spunbonded nonwoven (Figure 5)

In the surface layer we can clearly see the welding points, only a few defects in the shape of breakages, and delaminations surrounding the welding points. In the cross-section we can see that the metal covers only a few open layers, on one side, up to half of their cross-section, and with a thickness which lowers in the direction of the layer's edges. The maximum thickness of the sputtered metal layer was about 200 nm.

Screening efficiency

A measuring stand for measuring the screening activity was put into operation in 2005 in the Technical University of Wrocław. This stand enables us to measure flat materials in accordance with Standard D4935-99 [8]. This method allows direct measurements of the screening efficiency, in real time, of thin screening materials placed in a measuring cell. A net analyser may be used as a measuring device. which enables us to measure the insertion and return losses. The screening efficiency is determined as the difference between the attenuation level of a reference sample and the sample tested, considering insertion and return losses. Two samples in the shape of a disc of a diameter of 133 mm are necessary for the measurement. The screening efficiency was measured within the range from 30 MHz to 1.5 GHz. In practice, measurements are possible from about 1 MHz. The dynamic of the measuring device enables measurements of the screening efficiency up to 60 dB. The attenuation measurement results are presented in Table 2.

The values shown in the table for frequencies below 300 MHz are within the margin of error, considering that no calibration was performed. Over 300 Hz, the screening values for the Cu-V and Cu-PET samples are negligible. In the cases of the Cu-V and Cu-PET samples, the lack of screening may be caused by weak contact, which is also visible in the measurements of resistivity of the materials shown in Table 1, and on the basis of the microscopic pictures.

In such thin electro-conductive layers as those obtained, the screening efficiency is a function of the materials' conductivity and the layer thickness. If the screen is homogeneous, for example a foil of pure copper with conductivity of $S = 57.9 \times 10^6$ S/m, and of similar thickness, then the theoretical screening efficiency, measured as shielding attenuation (SA) within the range from 30 MHz to 1300 MHz, should be approximately constant, and equal:

for Cu thickness of 60 mm
SA = 56 dB,
for Cu thickness of 100 mm
SA = 61 dB, and
for Cu thickness of 200 mm
SA = 67 dB.

Increasing the screen thickness twice, we should achieve an increase in the attenuation of about 6 db, which means increasing the screening efficiency of the electromagnetic field's electrical component by a factor of two. A screen formed by the fibres coated with copper is not a tight screen, and therefore every time it will be characterised by worse screening properties than pure foil. Even if the

Table 2. Attenuation values for nonwoven samples sputtered with copper.

Frequency, MHz	Sample attenuation, dB		
	Cu-V	Cu-PET	Cu-Cu-PP
10	0.90	2.68	32.08
30	5.28	5.10	26.59
100	2.58	2.51	24.56
500	0.05	0.09	19.23
800	0.11	0.14	19.78
1000	0.26	0.36	16.85
1300	0.07	0.08	15.10
Thickness of the copper layer, nm	60	100	200

deposited layer is not tight, which would cause a decrease in the screening efficiency with an increase in frequency, the increase in the conductive layer thickness should result in an effect of attenuation increase within the range of 6 dB (while increasing the thickness twice). This will only occur on condition that the electrical conductivity of the screen does not change, which means that good contact of the copper-sputtered fibres would be maintained. This phenomenon should certainly be observed for copper up to a thickness of 1 μm. If a further increase in thickness occurs, the phenomena of multiple reflections and dispersions would be significantly important, as this will mean that a further increase in attenuation must not mean a proportional increase in the screening efficiency; the doubling in the layer thickness will not cause a doubling in the screening efficiency. It should be emphasised that the above-presented analysis is valid only for the frequency range which we used for testing samples.

The best screening efficiency of all the samples tested was stated for the copper-sputtered (Cu-PP) polypropylene nonwoven; the efficiency differed with the change in the frequency. We are conducting further research work concerned with optimising the sputtering process, process parameter selection, and choosing the best feature of the base.

Conclusions

As the result of this research work, we stated that the method of magnetron sputtering enables a metallic layer to be laid on textile materials. This technique has hitherto not been used for processing textiles.

The microscopic estimation of the copper-sputtered samples demonstrated that the arrangement of fibres and their density, especially on the surface layer, which depend on the nonwoven's manufacturing method, were decisive for the efficiency of the metal layer's penetration into the nonwoven's structure.

The sputtering tests carried out in laboratory conditions, at selected parameters for feeding the magnetron, demonstrated that it is possible to obtain materials with good screening efficiency; the best results were obtained with the Cu-PP nonwoven.

A decisive condition for obtaining a good-quality material is assuring the formation of a possible continuous metal layer on the fibres and good contact between the fibres.

This research will be continued within projects submitted to the Ministry of Science and the Higher Education.

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