DEPOSITION OF BIOCIDAL ZnO+Cu COATINGS USING HIGH-POWER PULSED MAGNETRON SPUTTERING TECHNOLOGY (HIPIMS)

[1]Joanna KACPRZYŃSKA-GOŁACKA, [1]Sylwia SOWA, [2]Piotr WIECIŃSKI, [1]Wioletta BARSZCZ, [1]Monika ŁOŻYŃSKA,

[1]Łukasiewicz Research Network – Institute for Sustainable Technologies, 6/10 Pułaskiego St., 26-600 Radom, Poland, EU, joanna.kacprzynska-golacka@itee.lukasiewicz.gov.pl

[2]Faculty of Chemistry, Warsaw University of Technology, 3 Noakowskiego str. 00-664 Warsaw, Poland, EU,

https://doi.org/10.37904/metal.2025.5140

Abstract

One of the most perspective directions of the surface engineering development in recent years concerns the possibility of producing coatings with bactericidal properties. For this purpose modern plasma technologies are used. Due to the very large possibilities in shaping the chemical composition of coatings, their microstructure and thickness, as well as the large variety of their deposition methods, they will enable the production of coatings with various functional properties. In recent years, it has become a completely new approach to design functional coatings on the surface of polymer filtration membranes to give them biocidal properties. The article presents the possibilities of using the High Power Impulse Magnetron Sputtering HiPIMS technology to deposit composite coatings with biocidal properties. In the article, in addition to the results of the bactericidal properties, the authors also presented an analysis of the material properties (microstructure, phase composition), mechanical properties (hardness, Youngs module) and physicochemical properties (wettability) of the tested coatings. The presented results confirmed the very good biocidal properties of the ZnO+Cu coating against various groups of microorganisms (bacteria and fungi) simultaneously.

Keywords: Magnetron sputtering, composite coatings, bactericidal properties, fungicidal properties

1. INTRODUCTION

The magnetron sputtering method is a very well-known surface engineering technology and an effective technological tool in the process of manufacturing thin coatings with various functional properties. There are many different magnetron sputtering methods [1-3], which allow for the free composition of the chemical composition, phase composition and structure of the deposited coatings. Coatings created by this method are used in many applications, such as: anti-wear coatings for tools [4,5,6], anti-corrosion coatings for machine elements [7,8], or decorative coatings [9]. A completely innovative approach is the creation of functional coatings on the surface of polymer filtration membranes to give them new application properties. Among the currently used material solutions for the surface layer used to impart properties that are important in the filtration process, i.e. hydrophilic and self-cleaning properties, the most commonly used coatings are those based on zinc oxides. These coatings are characterized by good hydrophilic, self-cleaning and photocatalytic properties [10,11]. It should be remembered that coatings based on titanium oxide or zinc oxide have relatively low bactericidal activity. Literature analysis has shown that their doping with various metals helps to improve functional properties. Studies on TiO_2, TiO_2+Cu, TiO_2+AgCu and ZnO+Zn coatings have shown that the addition of metals significantly improved the bactericidal properties against both gram-positive (G+) and gram-negative (G-) bacteria. Such wide possibilities in shaping the functional properties of surfaces make magnetron technologies of thin film deposition seem to be a promising method of shaping the functional properties of polymeric filter materials as well. This article presents the possibilities of using the High Power Impulse Magnetron Sputtering (HiPIMS) technology for the deposition of composite coatings based on ZnO doped with Cu. In the article, the authors compared the bactericidal, physico-chemical and mechanical properties of the

ZnO+Cu composite coating with a one-component ZnO coating. Moreover,the publication also presents an analysis of the material properties (microstructure, phase composition) of the ZnO+Cu coating. The presented results confirmed very good biocidal properties of the ZnO+Cu coating against various groups of microorganisms (bacteria and fungi)simultaneously.

2. EXPERIMENT

2.1. Preparation of coatings

The coating deposition processes were carried out using the HiPIMS (High- Power Impulse Magnetron Sputtering). The technological processes were realized by using the PVD-Standard-3 device, which is located at the Surface Engineering Centre in Łukasiewicz-Institute for Sustainable Technologies in Radom. Two TORUS 4 magnetrons from K.J. Lesker were installed on the wall of the chamber in the PVD-Standard-3 devices. For the process of coating deposition, two types of targets, Cu (99.99% purity) and ZnO (99.99% purity), with a diameter of 100 mm and a thickness of 7 mm, were used. The distance between the sample and the plasma source was 200 mm.

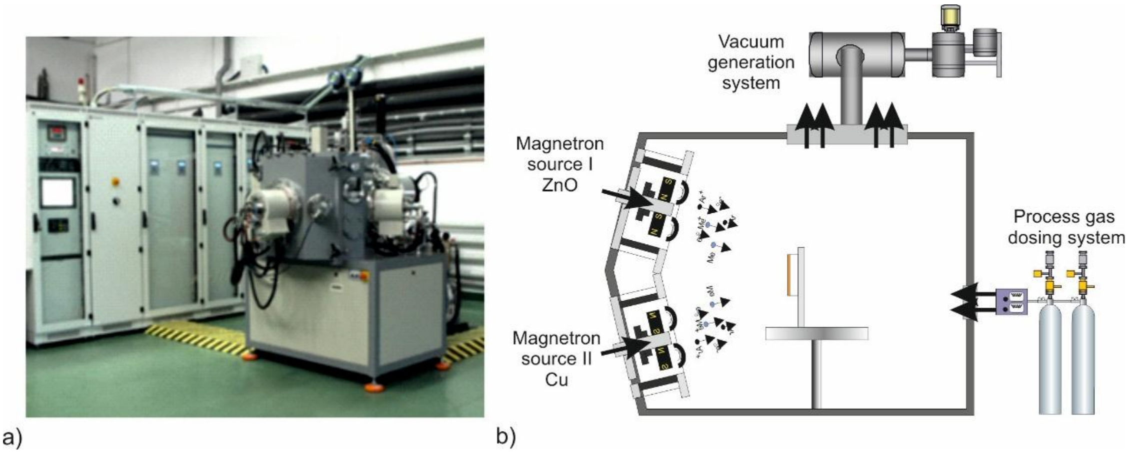


Figure 1 Technological device PVD-Standard-3 for the implementation of plasma surface treatment (a) and a scheme of the technological configuration enabling the implementation of magnetron sputtering processes in a two-magnetron system (b)

The samples were coated at room temperature. The coatings were produced without substrate polarization. The detailed parameters of the deposition process are presented in **Table 1**.

Table 1 Parameters of deposition for PVD-HiPIMS coatings

Materiał	Atmosphere [sccm]	Pressure p [mbar]	Magnetron source power P [W]	Temperature T [^{o}C]	Type of plasma source
Cu+ZnO	Ar:300	5.0 x 10^{-3}	Cu:100, ZnO:260	20	TORUS(Cu) and (ZnO)
ZnO	Ar:300	5.0 x 10^{-3}	ZnO:260	20	TORUS (ZnO)

Coatings were made on two types of samples for the study:

- Samples made of pure ARMCO with diameter ϕ = 25 mm, thickness = 6 mm and surface roughness= 0.05 μm were used for the analysis of the chemical composition, phase structure and microstructure of the coatings;
- POLYMER samples with a diameter ϕ = 25 mm, thickness g = 6 mm and surface roughness Ra = 0.05 μm were used for the analysis of wettability and antibacterial properties.

2.2. Coatings characterization

Microstructure was analysed using Helios 5 PFIB Xe scanning electron microscope with xenon ion sources and a TOF-SIMS detector. Chemical composition tests of the coatings were conducted using Energy-dispersive X-ray spectroscopy (EDS). Phase composition was carried out on an Empyrean DY1061 diffractometer equipped with a Cu lamp with an X-ray wavelength λ_{Cu}=1,54 Å, at a fixed angle of incidence, with the following parameters: 2 theta = 20° ÷ 100°, step = 0.03°, t = 12s, a = 3°. The mechanical properties of the coatings, such as hardness and Young's modulus, were investigated using the Anton Paar nanoindenter. The measurements were carried out with the Berkovich indenter in a single cycle using the following parameters: F=10mN, dF/dt=20mN/min.

For the investigation of the wettability of coatings, a static sessile drop method (drop volume of 2 µL) was used. For this purpose, the goniometer constructed at Łukasiewicz - ITeE (Radom, Poland) was used. For each sample, 10 measurements of the contact angle were taken, and then the mean value was calculated.

The microbiological resistance of the samples was tested by static contact under constant humidity conditions against two strains of bacteria: *Escherichia coli* (G+) *Staphylococcus aureus* (G-) and *Candida albicans* fungi. Each of the tested samples was sterilized in UV for 30 minutes and then inoculated with a microorganism inoculum from a 24- hour culture (in the case of bacterial strains) and a 48-hour culture (in the case of yeast strains) at a concentration of $1x10^8$ jkt/mL. The prepared samples were placed in an incubator in constant humidity conditions as follow: 37°C for bacteria (24h) and 30°C for yeast (48h). After the specified incubation time, the samples were placed in sterile flasks containing sterile phosphate buffer (0.25 M) and shaken for 5 min. At 180 rpm to isolate viable microbial cells. Then, the cultures were inoculated onto growth media plates and re-incubated at the appropriate temperature, depending on the strain tested by using the serial dilution method for a specific time. The same procedure was used for control samples. The test was repeated three times for all samples. After incubation, antimicrobial efficacy was determined according to the formula:

$$\mathbf{r[\%]=(Iw-Ip/Iw)x100\%} \qquad (1)$$

where

Iw-concentration of the initial inoculum of the microorganism;

Ip- concentration of the microorganism after contact;

Ip- concentration of the microorganism after contact with the tested sample.

3. RESULTS

3.1. Characterization of ZnO+Cu and ZnO coatings

The material analysis and physico-chemical properties of the ZnO+Cu and ZnO coatings are presented in (**Figures 2-5**) and **Table 2**, respectively.

a) b)

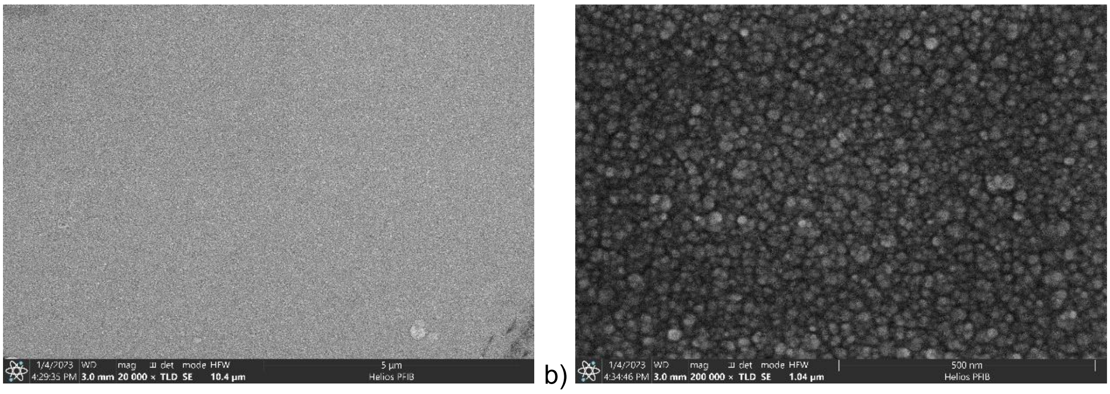


Figure 2 SEM observations of the surface of ZnO coatings produced by the HIPIMS a) magnification 20 000x, b) magnification 200 000x

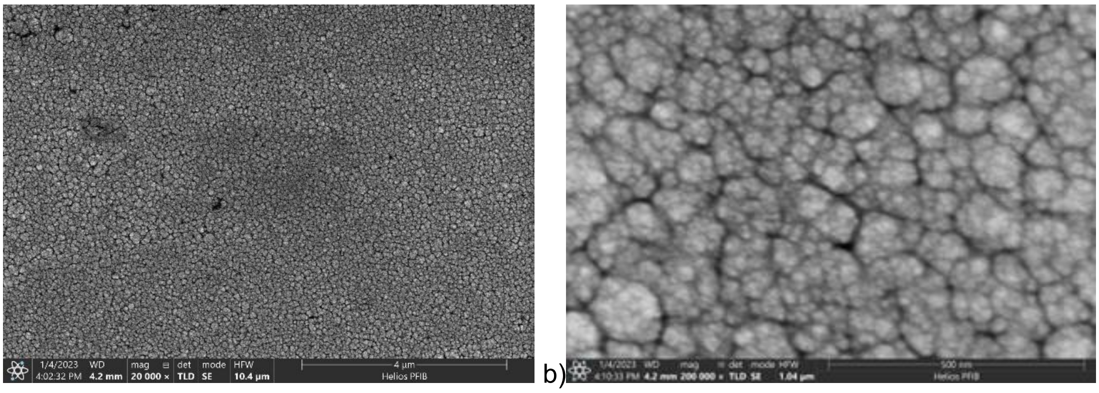


Figure 3 SEM observations of the surface of ZnO+Cu coatings produced by the HIPIMS
a) magnification 20 000x, b) magnification 200 000x

Figure 2 and **Figure 3** shows the results of SEM analysis of the morphology of ZnO and ZnO+Cu coatings. The surface observations showed that the ZnO coating has a homogeneous morphology and consists of spherical particles. The particle size was difficult to determine the exact. Their diameter it was in the range of 10-20 nm. The ZnO+Cu coating also consists of spherical shapes particles but in the form of agglomerates with a size of up to 100nm separated by coating discontinuities. The observed lower density of the ZnO+Cu coating will have a negative impact on the mechanical properties of this material. The thickness of the obtained coatings was similar and for ZnO is 1400nm and for ZnO+Cu is 1300 nm (**Table 2**). The phase structure analysis (**Figure 4**) confirmed that the deposited coating consists of two separate phases (a pure copper phase and a zinc oxide phase). The Fe peaks observed in the diffractogram come from the substrate and indicate high porosity of the deposited coating observed in the microscopic images (**Figure 4**).

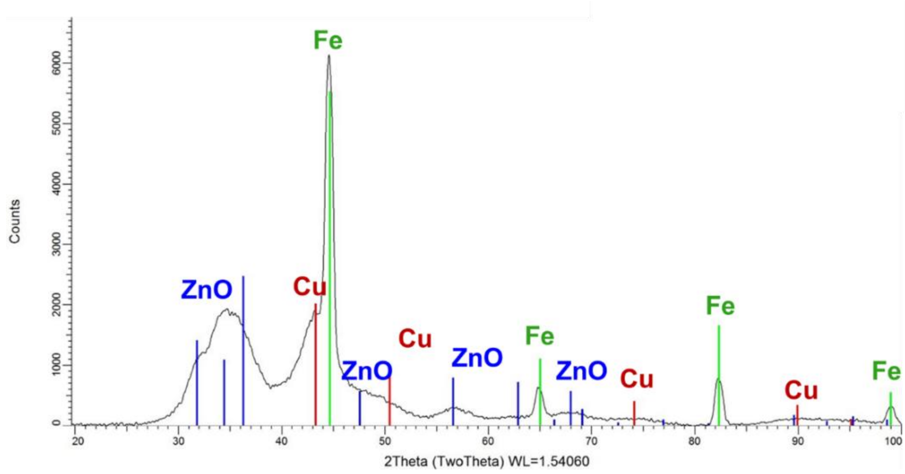


Figure 4 Phase composition of ZnO+Cu coatings

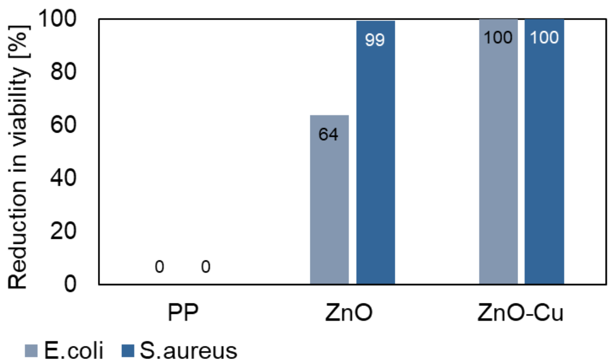
The chemical composition and other functional properties of the studied ZnO+Cu coatings, i.e. hardness, Young's modulus, ratio of hardness to elastic modulus (H/E) and plastic deformation coefficient (H^3/E^2), and wettability are presented in **Table 2**.

Table 2 The characteristic parameters: thickness, critical load, hardness, Young's modulus, H/E and H^3/E^2 for ZnO+Cu coatings compared to pure ZnO coatings

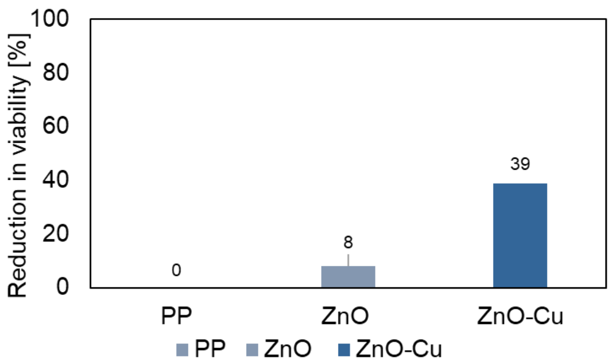
Coatings	Chemical composition [%At] Zn/Cu/O	Thickness [nm]	Hardness H [GPa]	Young's module E [GPa]	Plasticity Index H/E	Resistance to the plastic deformation H3/E2	Wettability [º]
ZnO+Cu	27/28/45	1300	3,9 ± 0,1	124 ± 6	0,031	0,003	74
ZnO	43/0/57	1400	9,0 ± 0,8	142 ± 5	0,063	0,036	60

The authors compared hardness and Young's modulus of ZnO+Cu ($H_{ZnO+Cu} \approx 3{,}9$ GPa, $E_{ZnO+Cu} \approx 124$ GPa) coating to pure ZnO coating ($H_{ZnO} \approx 9{,}0$ GPa, $E_{ZnO} \approx 142$ GPa). The presented results showed a 50% decrease in hardness and approximately 10% decrease in Young's modulus of the ZnO+Cu coating in comparison to one component ZnO coating. The deterioration in the stress-plastic properties was also observed. It can be caused by high copper content in the ZnO+Cu coating structure. To produce a material with better mechanical properties, the copper content should be reduced. The wettability analysis showed that the wetting angle of the ZnO+Cu coating in relation to demineralized water was 74^{o}, which indicated the hydrophilic character of the created coating. The wetting angle for the one- component ZnO coating was 60^{o}. This slight increase confirms that the addition of copper does not change the hydrophility of ZnO coating.

The biocidal properties of ZnO and ZnO+Cu coatings were analyzed against *Bacillus subtilis* (G+) and *Escherichia coli* (G-) and *Candida albicans* fungi (Figure 5). Analysis of the degree of microbial count reduction showed a 99% reduction of Gram (+) bacteria, a smaller 64% reduction of Gram (-) bacteria and only an 8% reduction of fungi for the one-component ZnO coating. The addition of copper to the ZnO coating resulted in a significant improvement of biocidal properties. The analysis of the degree of reduction of the number of microorganisms showed complete inhibition of the survival of Gram (+) and Gram (-) bacteria for the ZnO+Cu coating. Only in relation to fungi the biocidal effect of ZnO+Cu was limited and caused a 39 % reduction of *Candida albicans* fungi. However, this effect was more than four times higher than for ZnO coating.



a)



b)

Figure 5 Biocidal properties of ZnO+Cu multicomponent coatings produced by the HiPIMS compared to the pure ZnO coatings: a) reduction viability of *Bacillus subtilis* (G+) and *Escherichia coli* (G-) bacteria, b) reduction in viability of *Candida albicans* fungi

4. CONCLUSION

The research confirmed that the addition of copper to the ZnO coating resulted in a significant improvement in biocidal properties. In the case of ZnO+Cu coating, not only complete reduction of Gram (+) and Gram(-) bacteria was observed, but also a 40% reduction of fungi, which proves the universal biocidal properties of this material. The addition of copper did not cause any significant change in the hydrophilic properties. For ZnO+Cu coating, only a 20% increase in the wetting angle was noted compared to the one-component ZnO coating. This coating still exhibits hydrophilic properties. However, a negative influence of copper addition on the mechanical properties was observed. ZnO+Cu coating was characterized by twice lower hardness and a smaller Young's modulus, which also contributed to the deterioration of the elastic-plastic properties of the coating. The deterioration of mechanical properties is related to the lower density and observed porosity in the coating structure. The mechanical properties will not be of such importance because such a type of coatings could be used to improve the functional properties of polymeric filter materials. Taking into account the properties of coatings, which are important in the filtration process, i.e. hydrophilic and biocidal properties, the presented ZnO+Cu coating may prove to be a very effective solution for imparting universal biocidal properties for polymeric filtration materials.

ACKNOWLEDGEMENTS

This work was supported by the National Centre for Research and Development in Poland carried out within the project TECHMATSTRATEG III „Long-life composite filter media for water cleaning and high efficiency separation of gas-liquid and liquid-liquid dispersions", no. Techmatstrateg III/005/2019-00.

REFERENCES

[1] M.R.A. CRUZ, D. SANCHEZ-MARTINEZ, L.M. TORRES-MARTÍNEZ Optical properties of TiO2 thin films deposited by DC sputtering and their photocatalytic performance in photoinduced proces, Int J Hydrog Energy, 44 (2019), pp. 20017-20028, 10.1016/j.ijhydene.2019.06.043

[2] K. GRIGOROV, J. LIBARDI, R. MORAES, A.S. DA SILVA SOBRINHO, M.S. OLIVEIRA, D.M.G. LEITE, M. MASSIC, Titanium-dioxide nanostructures grown by dual DC/HiPIMS for dye-sensitized solar cell applications, Mater Res, 23 (2020), Article e20200218, 10.1590/1980-5373-MR-2020-0218

[3] P. NUNES, D. COSTA, E. FORTUNATO, R. MARTINS, Performances presented by zinc oxide thin films deposited by R.F. magnetron sputtering, Vacuum,2002, 64

[4] CZAPLA, K.; ŻABA, K.; KOT, M.; NEJMAN, I.; MADEJ, M.; TRZEPIECIŃSKI, T. Tribological Performance of Anti-Wear Coatings on Tools for Forming Aluminium Alloy Sheets Used for Producing Pull-Off Caps. Materials 2023, 16, 6465. https://doi.org/10.3390/ma16196465.

[5] FAGA M.G., SETTINERI L., Innovative anti-wear coatings on cutting tools for wood machining, Surface and Coatings Technology 2006, 201, https://doi.org/10.1016/j.surfcoat.2006.06.013.

[6] KACPRZYŃSKA-GOŁACKA, J.; SOWA, S.; BRUDNIAS, R.; PAĆKO, D.; SŁOMKA, Z.; PIASEK, A.; WIECIŃSKI, P.; HABRAT, W.; GARBACZ, H.; KOPIA, A.; et al. The Influence of nc-AlCrTiN/α-BN Coatings on Increasing the Durability of WC/Co Cutting Inserts in the Inconel Alloy Machining Process. Materials 2024, 17, 2587. https://doi.org/10.3390/ma17112587.

[7] CALDERON, S.; ALVES, C.F.A.; MANNINEN, N.K.; CAVALEIRO, A.; CARVALHO, S. Electrochemical Corrosion of Nano-Structured Magnetron-Sputtered Coatings. Coatings 2019, 9, 682. https://doi.org/10.3390/coatings9100682.

[8] LIU, Y.-C.; HSIAO, S.-N.; CHEN, Y.-H.; HSIEH, P.-Y.; HE, J.-L. High-Power Impulse Magnetron Sputter-Deposited Chromium-Based Coatings for Corrosion Protection. Coatings 2023, 13, 2101. https://doi.org/10.3390/coatings13122101.

[9] ARRUDA, A.C.S.D.; MANSANO, R.D.; ORDONEZ, N.; RUAS, R.; DURRANT, S.F. Ag Behavior on TiN Thin Films for Decorative Coatings. Coatings 2024, 14, 322. https://doi.org/10.3390/coatings14030322.

[10] M. HORPRATHUM, P. CHINDAUDOM, P. LIMNONTHAKUL, P. EIAMCHAI, N. NUNTAWONG, V. PATTHANASETTAKUL, A. POKAIPISIT, P. LIMSUWAN, Fabrication and Characterization of Hydrophilic TiO2 Thin Films on Unheated Substrates Prepared by Pulsed DC Reactive Magnetron Sputtering, Journal of Nanotechnology 2010, https://doi.org/10.1155/2010/841659.

[11] P. ZEMAN, S. TAKABAYASHI, Self-cleaning and antifogging effects of films prepared by radio frequency magnetron sputtering ,J. Vac. Sci. Technol. A 20, 388–393 (2002), https://doi.org/10.1116/1.1446445.