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STUDY OF THE EFFECT OF PROCESS DURATION ON THE PROPERTIES OF ZnO-Ag COATINGS DEPOSITED BY THE HIPIMS METHOD

Zinc oxide coatings commonly known for their biocidal properties were co-sputtered with metallic silver. Coatings were deposited on iron substrates with High Power Impulse Magnetron Sputtering (HiPIMS) method for the following durations: 5, 20, 40 and 60 minutes. The influence of deposition time on surface morphology, chemical and phase composition, surface roughness and wettability were evaluated. The results showed that silver segregation was observed on the surface of the coating, with the amount of silver increasing with process duration, while phase composition of all coatings remains consistent. Studies of surface properties show all the ZnO-Ag coatings have low roughness and are highly hydrophobic, with slight increase of the values of these parameters with deposition time.

Keywords: Coating; zinc oxide; silver; HiPIMS

1. Introduction

Widespread access to antibiotics over many years has led to the emergence of numerous strains of pathogens that are resistant to their effects. Recent studies also show that global warming carries the risk of developing antibiotic-resistant strains transport of drinking water [1]. Considering such risks, there is a significant need to develop materials with biocidal properties worldwide. However, these materials must have the appropriate mechanical and functional properties to ensure their safe use, especially if they are intended for medical applications. A common approach is to modify the surface of materials to provide them with selected properties [2]. In this case, surface engineering is particularly effective. A good example is the application of particle-reinforced composite coatings containing metals with biocidal properties, such as silver [3]. Among the most used biocidal metal oxides are ZnO [4], TiO_2 [5], and CuO [6], which have been extensively studied due to their strong antimicrobial activity and chemical stability [7].

The combination of biocidal metal oxide with a biocidal metal has several advantages. For instance, an oxide matrix exhibiting photocatalytic properties may impart additional self-cleaning functionality to the antibacterial coating [8]. The key benefit of this combination is that it expands the spectrum of biocidal properties, as the materials complement each other, creating a synergistic effect [9]. Despite the many advantages associated with combining biocidal oxides and metals, there are also certain difficulties in their production. In the case of coatings deposited using PVD methods, the undesirable phenomenon of metal segregation may occur [10].

One of the most promising techniques of coatings deposition is High Power Impulse Magnetron Sputtering (HiPIMS). This method enables deposition of coatings with a compact and homogeneous microstructure, which also possesses biocidal properties. By selecting the process parameters, it is possible to control the dynamics of nucleation and, consequently, the morphology and structure of the coatings [11,12].

In this study, ZnO-Ag coatings were deposited using the HiPIMS method in four different process durations: 5, 20, 40 and 60 minutes. Subsequently, the effect of deposition time on the structure and properties of the coatings was investigated.

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2. Materials and methods

2.1. Samples preparation

ZnO-Ag coatings were prepared on iron substrates (25.4 mm diameter and 6 mm height) by the High Power Impulse Magnetron Sputtering (HiPIMS) method. Two magnetrons were equipped with 4'' targets made of pure silver (99.9% purity) and zinc oxide (99.9%). To obtain high-quality, homogeneous coatings using the HiPIMS method, process parameters were controlled. In HiPIMS mode the targets were operated with the pulse duration time of 50 μs and repetition frequency of 1000 Hz. The process atmosphere consisted of 100% argon, and the pressure in the chamber was maintained at 5.0×10^{-3} mbar. The coatings were deposited without substrate heating. The power setting on the magnetron was 100 W for silver and 260 W for zinc oxide, respectively. ZnO-Ag coatings were deposited at four distinct process durations: 5, 20, 40 and 60 minutes.

2.2. Material characterisation

Surface morphology observation, TEM lamella preparation, STEM imaging, and chemical analysis were carried out using a Thermo Scientific Helios 5 PFIB CXe field-emission scanning electron microscope (FE-SEM) equipped with a xenon (Xe) plasma-focused ion beam (FIB) column and an Octane Elite EDS detector. Surface morphology was characterised using the secondary electron signal (TLD detector) at a low accelerating voltage of 5 kV and a beam current of 25 pA. Prior to lamella preparation, the region of interest was coated with a protective platinum (Pt) layer to minimize surface damage during ion milling. Lamella cutting and thinning were performed at an accelerating voltage of 30 kV with progressively reduced beam currents (60 nA, 15 nA, 4 nA, 1 nA, and 0.3 nA). Final polishing was conducted at a reduced accelerating voltage of 5 kV. STEM imaging was performed at 30 kV using a STEM3+ detector. Based on SEM images, a quantitative analysis of silver particles on the surface, specifically their number and diameter, was performed. Chemical analysis, including area and line scans, was carried out at an accelerating voltage of 15 kV. Phase composition of deposited coatings was performed with the use of X-ray diffractometer Bruker D8 Advance (goniometer radius 280 mm) equipped with parallel optics and a Cu Kα radiation source (λ = 0.154056 nm). This equipment operates at a voltage of 40 kV and a current of 40 mA. The scanning optics elements consist of a Göbel mirror on the incident beam side and two secondary Soller slits in the diffracted beam. The measurements were performed at a constant primary beam angle of incidence of 1° in the 2θ range from 15° to 100°, with a step of 0.025° and a counting time of 3 s per step. To perform phase identification the Diffrac.Eva software (Bruker AXS, Karlsruhe, Germany) connected with X-ray diffraction data from the PDF-2 database (ICDD) was used. Surface roughness examination was performed using an optical profilometer WYKO NT9300. To quantify roughness, the Ra parameter (arithmetical mean height) was determined by two different magnifications (5×, 100×) using Gwyddion software. The wettability of the samples was tested using a DataPhysics OCA 25 goniometer, by the sessile drop method using distilled water, with the volume of each drop fixed at 0.8 mL.

3. Results and discussion

3.1. Surface morphology

The SEM images show the surfaces of the prepared ZnO-Ag coatings with deposition times of 5, 20, 40 and 60 minutes. Surface morphology investigations revealed the presence of bright particles on the surface of all coatings. Analysis of the surfaces at the lowest magnification (Fig. 1) indicates that the number of particles increases with the duration of the deposition process. Examination of surface morphology of coatings deposited with shorter process duration 5, 20 min (Fig. 1a,b) shows that the average particle size is smaller (19.3 nm and 25.3 nm) compared to coatings deposited with longer process duration as shown in Fig. 1c,d (59.4 nm and 60.6 nm). In the case of coatings deposited with time 5 and 20 min, the maximum particle size remains comparable, however, a higher number of bright particles is observed in coating deposited in 20 min. The same trend is observed in coatings deposited with longer process duration (40, 60 min), where the largest particles remain similar in size, while their content increases in accordance with the duration process.

A quantitative analysis of the particles visible on the surface of the coatings showed that their surface coverage was 3.2, 7.1, 26.7, and 29.6%, respectively, for deposition times of 5, 20, 40, and 60 minutes. As the duration of the process increases, the proportion of bright particles on the surface rises, with the largest increase observed between the coatings created in 20 and 40 minutes. Although observations were performed using secondary electrons, the contrast between bright particles and darker matrix is not related to topography, but to differences in density, conductivity and work function. Thus, it seems that bright particles are made of silver, while matrix is ZnO. To confirm that statement, chemical analysis was performed.

For the coating deposited for the longest duration (60 min), a linear analysis of the chemical composition was conducted along its cross-section from the surface toward the substrate. The EDS analysis showed that the amount of silver on the coating's surface is significantly higher compared to its concentration in deeper areas of the coating (Fig. 2). This confirms that the particles visible on the coating's surface (Fig. 1) are composed of silver. The thickness of the analysed coating was approximately 1 μm. The silver particles observed on the surface are much larger than those embedded inside the coating. Fig. 2b also shows the coating's microstructure beneath Ag particles, consisting of nanometric grains, most likely a mixture of ZnO and Ag. These observations suggest that the silver particles visible on the surface formed as a result of silver diffusion from the interior of the coating and segregation at the surface.

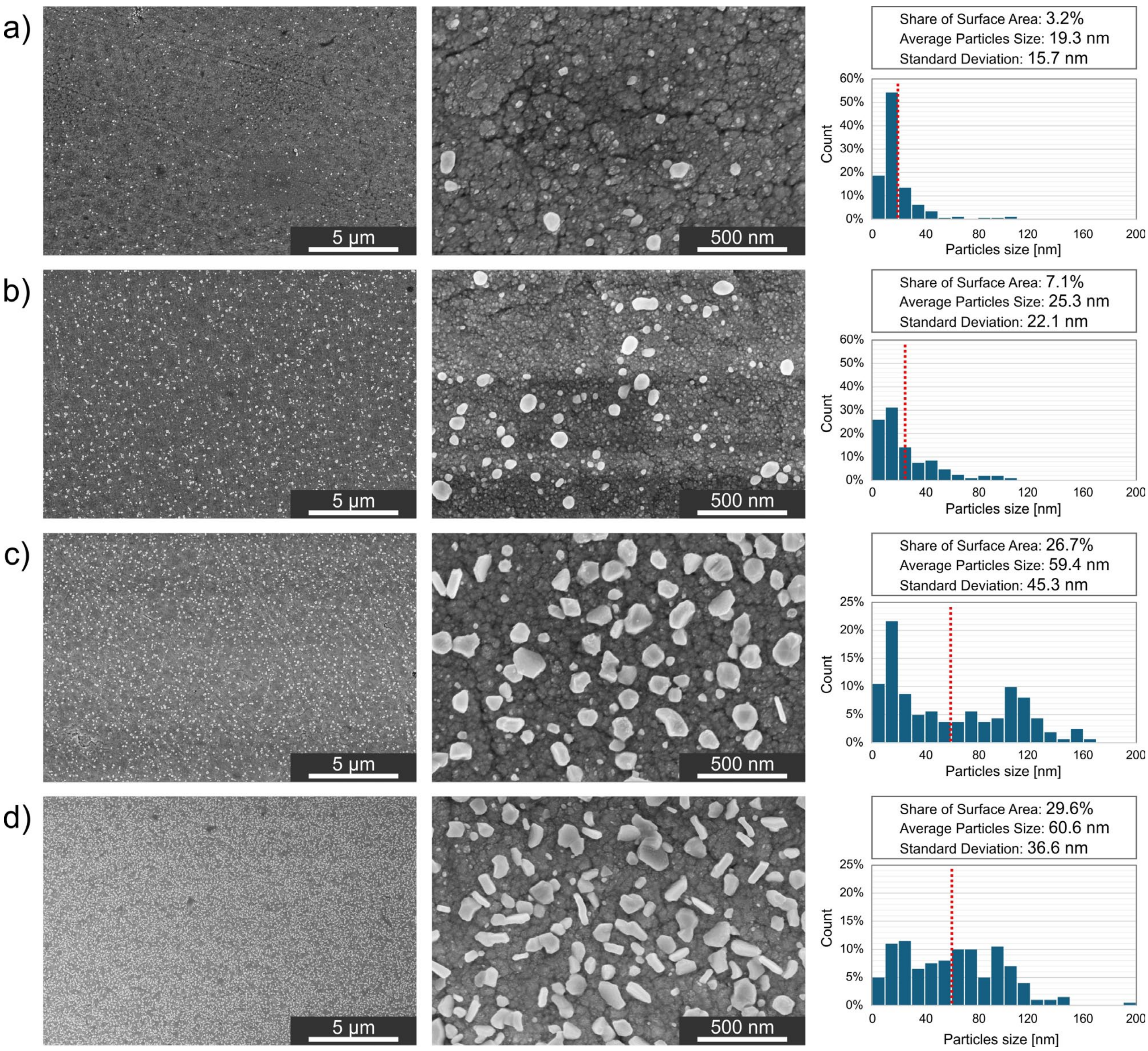

Fig. 1. Surface morphology and quantitative particle analysis of ZnO-Ag coatings deposited with process durations: a) 5 min, b) 20 min, c) 40 min, d) 60 min

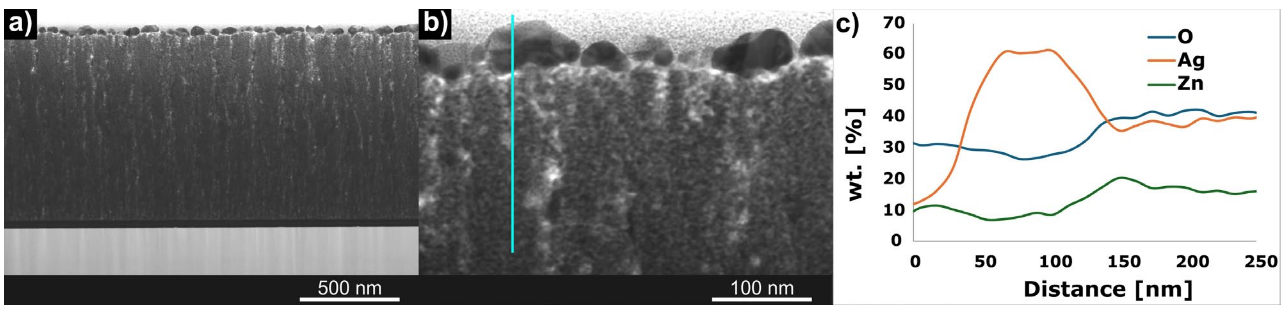

Fig. 2. Cross-section of the ZnO-Ag coating deposited in 60 min: a) magnification 100 000×, b) magnification 500 000×, c) linear analysis of the chemical composition along a cross-section

Deposition process of ZnO-Ag coatings results in silver segregation on the surface and amount of silver increases with time duration of deposition process for 5, 20, 40, 60 min, respectively. The impact of this phenomenon on the bactericidal properties of coatings will be the subject of our further research.

3.2. Chemical and phase composition

The elemental analysis of the deposited coatings, performed using the EDS method, is shown in Fig. 3. Due to the small particle sizes, below the resolution of this method, it was difficult to perform a point analysis. The chemical composition analysis of surface areas showed that the lowest silver content is found in the coating deposited in 5 min, while for the coatings deposited in longer durations Ag concentration significantly increases. There is a clear trend indicating that a longer process duration leads to more silver on the surface, and this is associated with a higher proportion of bright particles on the surface. The zinc content in the coatings is stable, although a slight decrease in its concentration can be observed as the process duration increases. The stronger decrease in oxygen content compared to zinc may additionally be related either to changes in the ZnO stoichiometry with increasing deposition time, as well as geometrical or topographical effects, to which the quantitative determination of light elements is particularly sensitive in EDS analysis.

In order to analyse phase composition of coatings deposited with 4 different time durations, low-angle X-ray diffraction was performed (Fig. 4). The analysis confirmed the presence of a metallic silver phase, characterised by strong and distinct reflections. All coatings exhibit diffraction peaks corresponding to the same crystalline phases regardless of the process duration. This indicates that the qualitative phase composition remains stable during the process. Low intensity of peaks originating from ZnO is most likely related to the fact that ZnO phase in the coatings is nanocrystalline, which leads to significant broadening and reduction of diffraction peak intensity. Sputtered ZnO coatings are often non-stoichiometric and contain a high density of structural defects and internal stresses generated during the deposition process. These factors may further broaden and weaken the ZnO reflec-

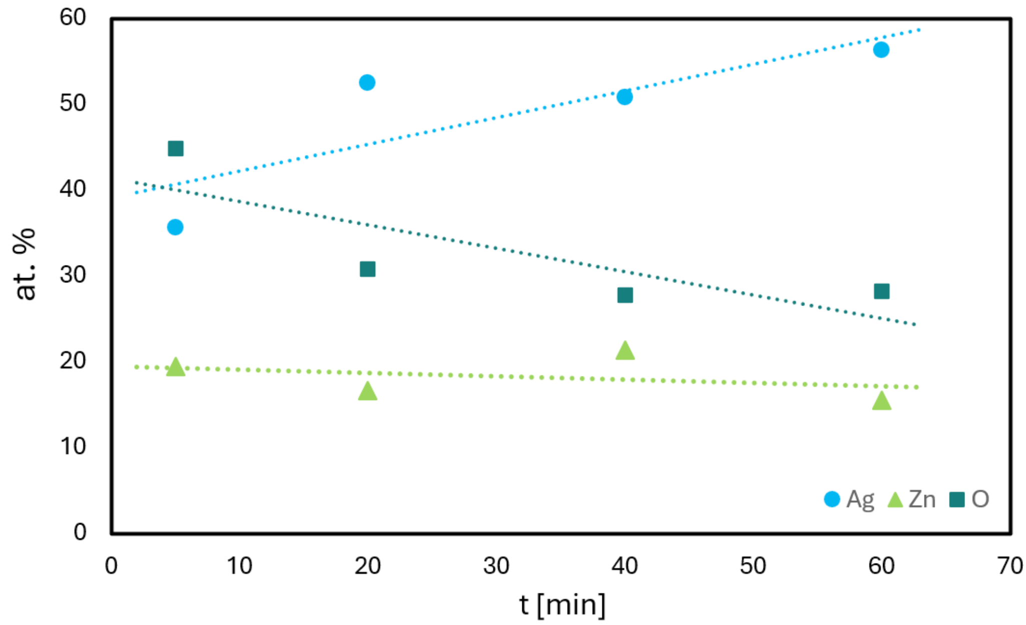

Fig. 3. Chemical composition analysis of ZnO-Ag coatings for different deposition times

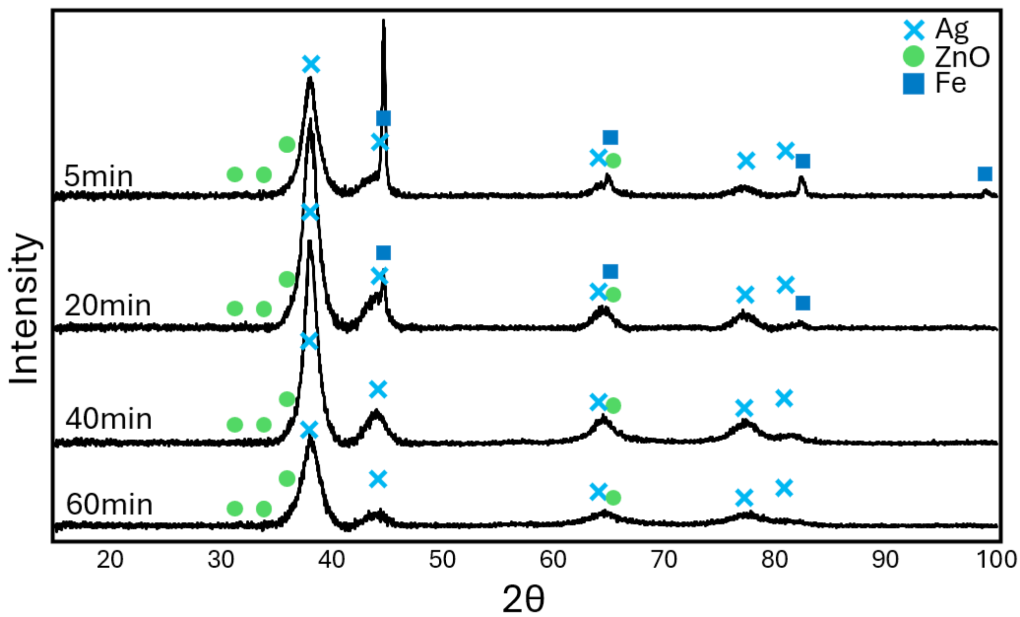

Fig. 4. Phase composition of ZnO-Ag coatings deposited for 5, 20, 40, 60 min

tions, making them difficult to distinguish from the background. Silver forms relatively large crystalline particles on surface with strong diffraction intensity, which additionally dominates the XRD patterns and masks the weaker ZnO reflections. However, in the enlarged section of the diffractogram (Fig. 4), very weak ZnO reflections indexed to the (100) and (002) lattice planes are visible. Furthermore, the asymmetry of the Ag (111) peak suggests the presence of an overlapping weak ZnO reflection originating from the (101) plane. Despite the application of low angle XRD, the influence of the substrate is still noticeable in the diffraction patterns for coatings deposited in 5 and 20 min, meanwhile patterns of coatings created in 40 and 60 min do not show any characteristic peaks for iron. This shows that the thickness of the coatings deposited at the shortest process durations is sufficiently low to allow the detection of peaks originating from the substrate material in the diffraction patterns and reveals that the thickness of the coatings increases with deposition time.

Analysis of the surface morphology, elemental and phase composition indicates that, even when identical deposition parameters are maintained, the resulting coatings may differ in Ag content and surface morphology. This represents a significant challenge in the design of such composite coatings with biocidal properties, for which both structure and performance must be controlled.

3.3. Roughness

The overall roughness of all examined coatings is very low, and the Ra parameter remains in the nanometer range. The roughness of the coatings surfaces was measured for two different areas (1300×940 and 63×47 µm). The values of Ra parameter of the tested coatings are shown in Fig. 5 and topography maps of the characterised samples are provided in Fig. 6. For measurements performed at higher magnifications, the surface roughness remains quite consistent and varies around 4 nm. However, at lower magnifications, a slight increase in roughness can be observed as the process duration increases. This means that an increase in the number of silver particles on the coating surface causes a higher degree of topographical development.

Sample	Roughness Ra [nm]	
t [min]	Magnification 5x	Magnification 100x
5	7.4	4.8
20	11.5	3.1
40	14.1	4.2
60	14.2	5.5

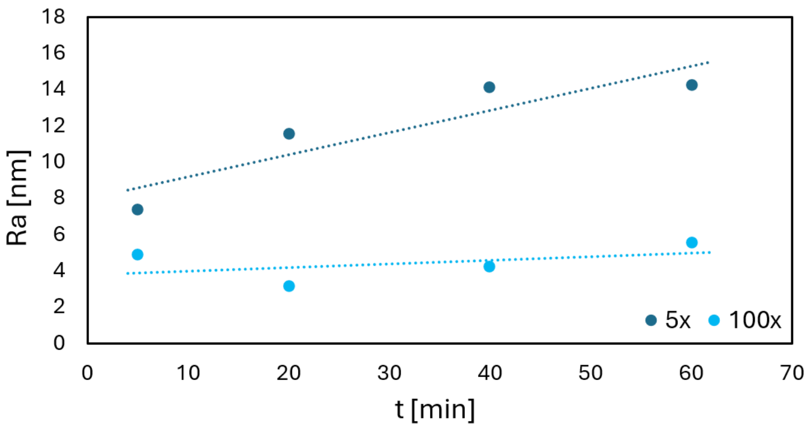

Fig. 5. The values of Ra parameter of coatings

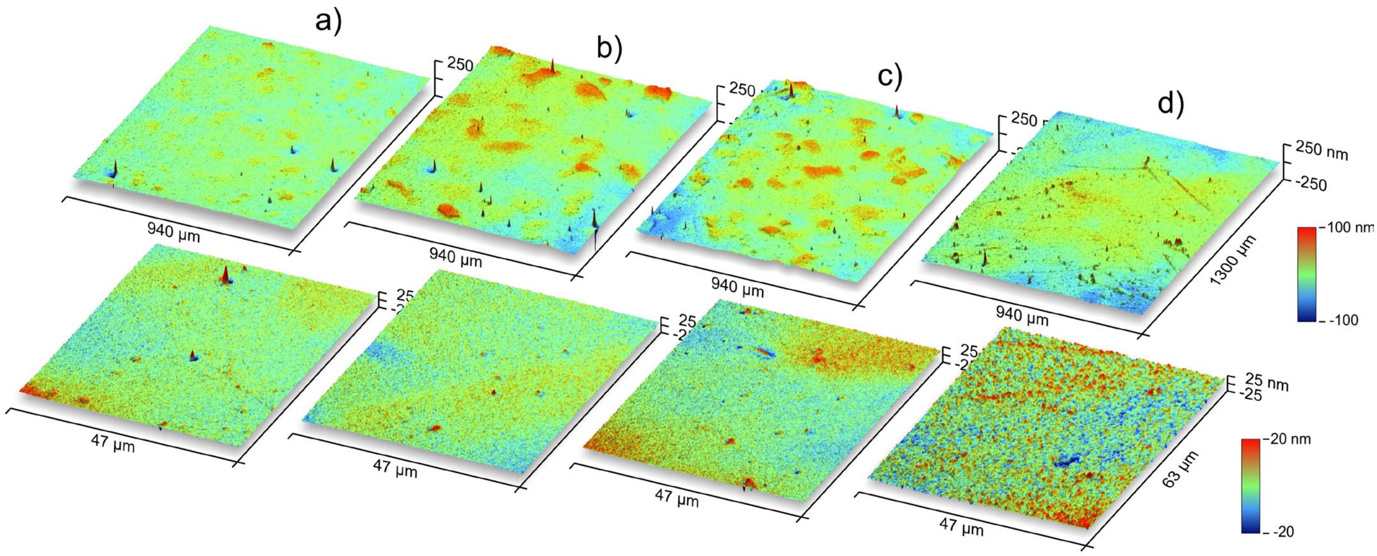

Fig. 6. Topography maps of the characterised coatings deposited with process durations: a) 5 min, b) 20 min, c) 40 min, d) 60 min

Sample	Wettability angle [°]
t [min]	Water
5	102.2
20	106.4
40	113.1
60	126.6

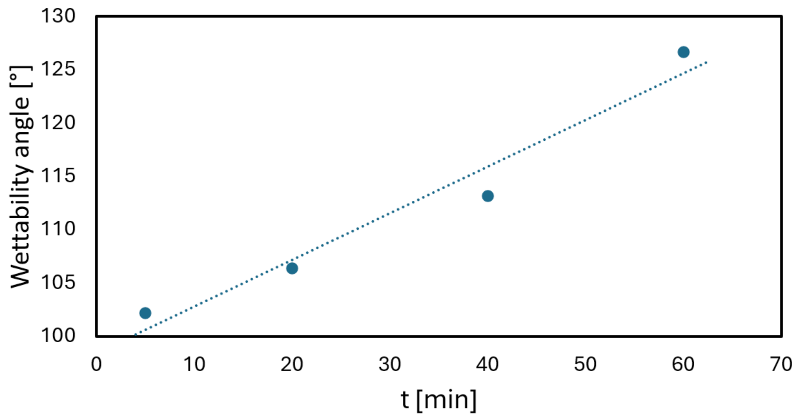

Fig. 7. The evolution of wettability angle of tested ZnO-Ag coatings

3.4. Wettability angle

A study of the wettability of the coatings using the sessile drop method showed that all coatings are hydrophobic, as the contact angles for each of them were higher than 90° [13]. The contact angle values increase as the coating deposition time increases (102.2°-126.6°) (Fig. 7), which indicates that the trend is consistent with the results of the roughness measurements, which also show a slight increase with the deposition time. This means that as the duration of the process increases, both the roughness and the hydrophobicity of the coatings increase.

Coatings of this type exhibit strong biocidal properties resulting from the synergistic interaction between their hydrophobic properties and the biocidal properties of the silver. Typically, superhydrophobic surfaces without a bactericidal additive exhibit weak biocidal properties, while superhydrophobic surfaces with a bactericidal additive exhibit extreme hydrophobic properties and rapid bactericidal action through the release of Ag ions [14]. Results of this study reveal that an increase in the proportion of silver particles on the surface enhances hydrophobic properties and may result in increased biocidal properties due to the synergy between the mechanism of weakening bacterial adhesion to the surface and the release of metal ions.

4. Conclusion

The present study investigated the influence of the process duration on the properties of ZnO-Ag coatings deposited by the HiPIMS method. The roughness, topography, microstructure, chemical and phase composition of the coatings, as well as their physicochemical properties (wettability) were analysed. Based on studies conducted, the following conclusions can be drawn:

1. The HiPIMS process allows to obtain hydrophobic, compact, and low-roughness ZnO-Ag composite coatings. The chemical and phase composition of all tested coatings confirmed the presence of ZnO and Ag, and no undesirable phases were detected. All this indicates the stability of the deposition process across different durations.
2. The silver particles observed on the surface formed as a result of silver diffusion from the interior of the coating and segregation at the surface. The impact of silver segregation on biocidal coatings properties will be the subject of the further analysis.
3. The duration (5, 20, 40 and 60 min) of the HiPIMS deposition process significantly influences the microstructure and properties of the ZnO-Ag coatings, with longer deposition times leading to increased: thickness, surface roughness in nanoscale and segregation of Ag on the surface. Both the particles size (19.3, 25.3, 59.4, 60.6 nm) and surface coverage (3.2, 7.1, 26.7, 29.6 %) of silver increased with process duration.
4. Contact angle measurements showed that the wettability of the coatings is affected by process duration; increased roughness generally led to enhanced hydrophobic behaviour, suggesting tunable surface properties.

To summarize, adjusting the HiPIMS process duration provides an effective means of tailoring the microstructure and physicochemical properties of ZnO-Ag coatings for potential functional applications.

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