ANALYSIS OF THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF OXIDE COATINGS PRODUCED BY RF- MS AND HIPIMS

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Abstract

The DC-MS magnetron sputtering method is a well-known surface engineering technology and is a very effective technological tool in the processes of producing multi-component coatings. One of the limits of DC magnetron sputtering is the production of metal oxide coatings. Mainly due to the insulating properties of targets made of metal oxides. Currently, the most widely used type of magnetron sputtering, which enables deposition of metal oxides coating, is High Power Impulse Magnetron Sputtering (HPIMS) and Radio Frequence Magnetron Sputtering (RF-MS). This method is characterized by high power density, high ionization and high plasma density, which enables the production of high-quality multi-component coatings. As part of the presented work, the characteristics of the material and functional properties of MeO coatings produced with the use high-power pulsed magnetron sputtering (HPIMS) and radio frequence magnetron sputtering (RF-MS) and were carried out. The mechanical and material properties of the produced coatings were compared. The conducted analysis showed a significant influence of the applied technology on the deposition rate and mechanical properties of the obtained materials.

Keywords: PVD, metal oxides coatings, magnetron sputtering, HIPIMS, RF-MS

1. INTRODUCTION

The magnetron sputtering method is a well-known surface engineering technology and a very effective technological tool in the process of producing thin coatings with various functional properties. Many different magnetron sputtering methods are known, which allow the chemical composition, phase composition and structure of the produced coatings to be freely composed. One of the types of coatings for which the magnetron sputtering method is used are coatings based on metal oxides such as AgO [1], CuO [2,3] or ZnO [4], which have become very popular in recent years. These coatings have very good biocidal properties and are used in many areas of industry. The most common methods are used to produce oxide coatings is High Power Impulse Magnetron Sputtering (HPIMS) and Radio Frequence Magnetron Sputtering (RF-MS). This method is characterized by high power density, high ionization and high plasma density, which enables the production of high-quality multi-component coatings. Therefore, RF magnetron sputtering and HiPIMS offer unique advantages for fabricating thin-film MeO coatings due to their ability to precisely adjust growth parameters to control the physical properties, microstructures, and film chemistries. In addition, the deposition process can be performed at lower substrate temperatures due to the addition of energy from low-energy particles bombarding the thin films [5-7]. The aim of this study is to compare the properties of ZnO deposited by means of two different methods, i.e. HiPIMS and RF-MS. In this work, all produced coatings are analyzed in terms of their surface morphology adhesion and mechanical properties.

2. EXPERIMENT

2.1. Preparation of coatings

The authors selected three different magnetron sputtering methods to deposit the tested coatings, i.e. (1) the high impulse magnetron sputtering method (HIPIMS) and (2) radio frequency magnetron sputtering (RF-MS). For the purpose of the analyses, Standard 3 (**Figure1a**), a specialized research device developed at Łukasiewicz Research Network – Institute for Sustainable Technologies (Ł-ITeE, Radom, Poland), was used to implement the technological processes of producing ZnO coatings using different type of power supply. The developed technological configuration is shown in (**Figure 1b**). The device has a plasma source located on the wall of the chamber. For the process of ZnO coating deposition, ZnO sputtering target (99.99% purity) with the diameter of 100 mm and thickness of 7mm, produced by Lesker, was used. The distance between the sample and the plasma source was 200 mm.

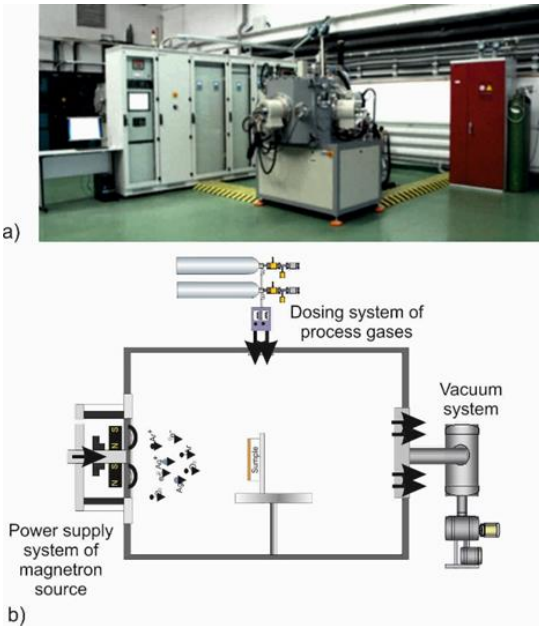


Figure 1 Standard 3 device for plasma treatment processes (a) and scheme of the technological configuration, which enables the implementation of magnetron sputtering processes in a single-magnetron system (b).

The samples were coated at room temperature and in argon atmosphere. The process of ZnO coating deposition was carried out at constant pressure, variable argon flow, which was adjusted to the thermodynamic conditions of the process, fell into the range from 290 to 300 sccm (cm3/min). An MKS working atmosphere control system was installed in the Standard 3 device, which enabled precise control of gas flows while maintaining a constant pressure in the working chamber. Process parameters of deposition the coatings are shown in **Table 1.**

Table 1 Technological parameters of deposition process of multicomponent ZnO coatings on the silicon and polypropylene surface.

Coatings	**Power** P_{ZnO} **[W]**	**Pressure p [mbar]**	**Working atmosphere**	**Time t [min]**
ZnO_{HiPIMS}	200	$5x10^{-3}$	100%Ar	100
ZnO_{RF-MS}	100	$5x10^{-3}$	100%Ar	120

2.2. Coatings characterization

The microstructure and surface morphology of the coatings were characterized with the use of SEM Hitach 3000 scaning microscope. The microstructure observations were carried out on a properly prepared sample in the form cross-section sample. 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. Adhesion parameters were measured with a scratch-test method with the use of the Revetest equipped with the diamond Rockwell indenter designed by CSM Instruments. The indenter's load force increased linearly in the range of 0-200 N, and the loading rate was 10N/min. Based on the changes in the acoustic emission and friction force, three critical load forces were determined corresponding to the major coating damage failure: Fc2 – adhesion defects, Fc3 – removed coating from all breadth of scratch. References

3. RESULTS

3.1 Morphology and chemical composition studies.

Figure 2 shows the results of SEM analysys of the deposited ZnO coatings. The surface observations showed that both coatings have a smooth and homogeneous structure.

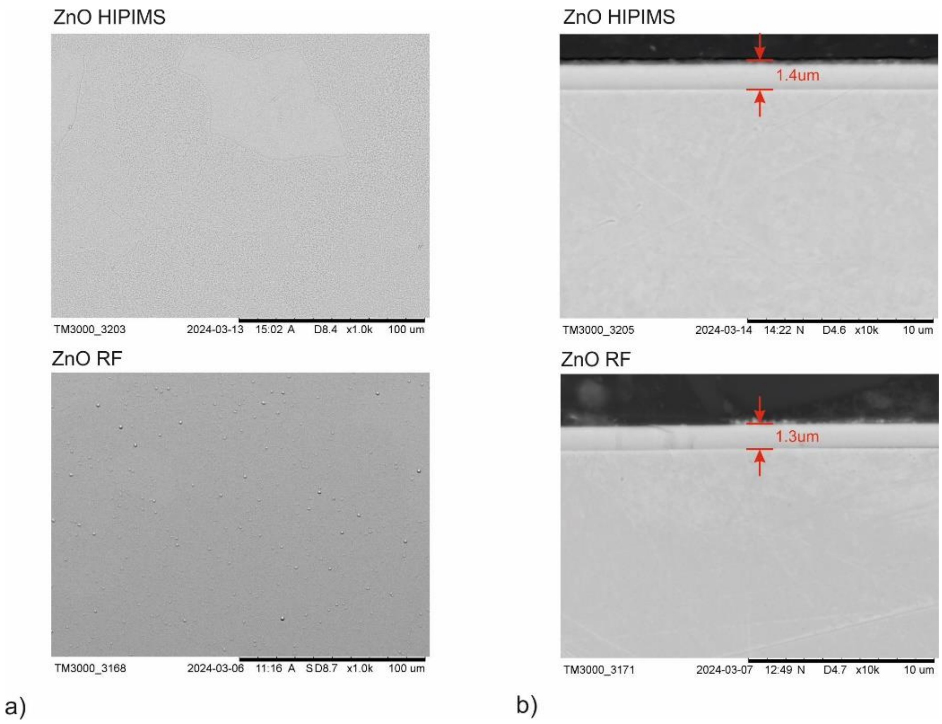


Figure 2 SEM observations of the surface (a) and cross-sections (b) of ZnO coatings produced by the HIPIMS and RF method.

The deposition rate determined on the basis of thickness measurements and the roughness parameters of the obtained coatings are presented in **Table 2**. The obtained results confirm that both coatings are characterized by similar deposition rate and surface topography.

Table 2 Deposition rate and roughness parameters of deposition ZnO.

Coatings	**Deposition rate [µ/h]**	**Roughness [µm]**		
		Ra	**Rz**	**Rt**
ZnO_{HiPIMS}	0,70	0,03	0,18	0,41
ZnO_{RFMS}	0,78	0,02	0,25	0,44

The chemical composition of the obtained coatings was also analyzed by means of energy-resolving EDS X-ray spectroscopy. **Figure 2** shows the chemical composition of ZnO coatings. The chemical composition analyzes showed that ZnO coatings deposited using both the HIPIMS and RFMS methods are characterized by similar chemical composition.

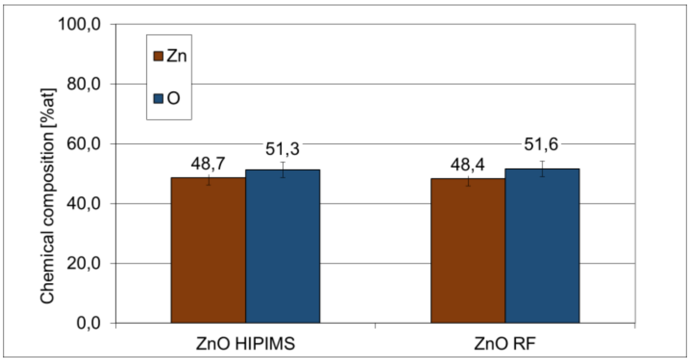


Figure 3 Chemical composition of ZnO coatings produced by the HIPIMS and RF method.

The SEM microscopic observations of the surfaces and cross-sections as well as the analysis of the chemical composition showed that ZnO coatings deposited using the HIPIMS and RF methods have similar parameters. No differences were observed in the surface topography, deposition rate or chemical composition of the obtained materials.

3.2 Mechanical properties studies

Mechanical properties of the studied ZnO coatings, i.e. hardness, Young's modulus, ratio of hardness to elastic modulus (H/E) and plastic deformation coefficient (H3/E2), are presented in **Table 3**.

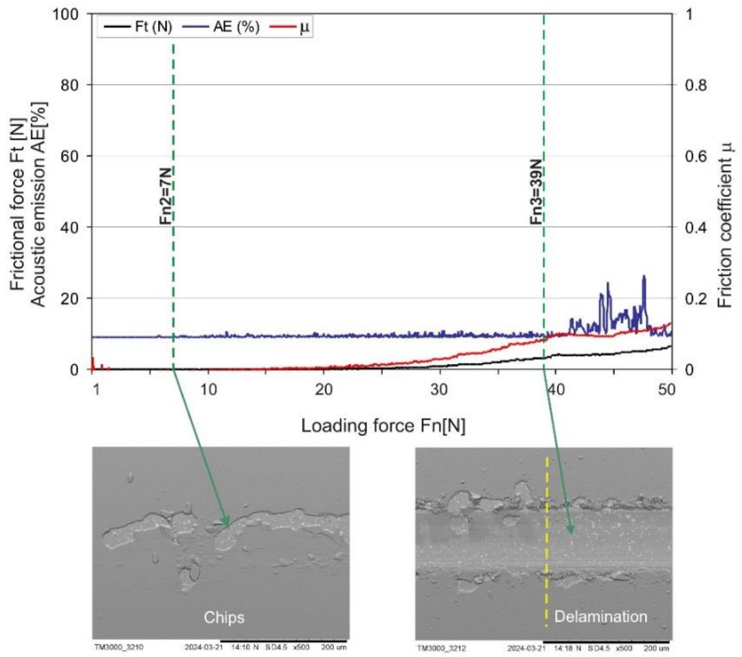
Table 3 Mechanical parameters of deposition ZnO.

Coatings	**Hardness H [GPa]**	**Young's module E [GPa]**	**H/E**	**H3/E2**
ZnO_{HiPIMS}	9,0 ± 0,8	142 ± 5	0,063	0,036
ZnO_{RFMS}	7,7 ± 0,6	167 ± 6	0,047	0,017

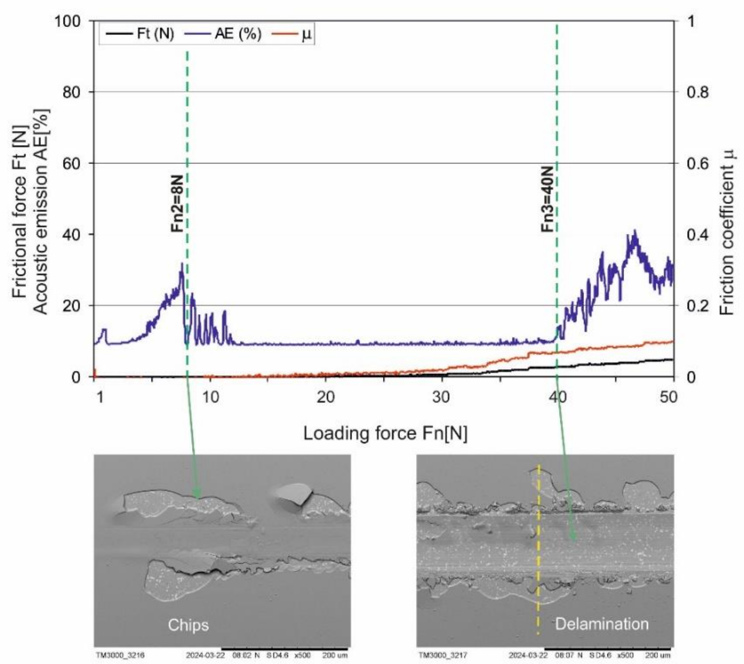
The authors indicated that the produced coatings have hardness $H_{ZnO\text{-}HiPIMS} \approx 9{,}0$ GPa, $H_{ZnO\text{-}RFMA} \approx 7{,}7$GPa, and Young's modulus $E_{ZnO\text{-}HiPIMS} \approx 142$ GPa, $E_{ZnO\text{-}RFMA} \approx 157$GPa. Varying hardness and Young's modulus values affect the elastic and plastic properties of the produced coatings, including elastic strain (H/E) and resistance to plastic deformation (H^3/E^2). The analyses show that the ZnO_{HIPIMS} coating, for which the H/E and H^3/E^2 ratios are higher than in the case of the ZnO_{RFMS} coating, has better elastic and plastic properties. This means that the ZnO_{HIPIMS} coating is more resistant to crack initiation than the ZnO_{RFMS} coating.

3.3 Adhesion studies

Results of adhesion tests for ZnO coatings prepared by different deposition method (HiPIMS and RFMS) are presented in (**Figure 4a and 4b**).



a)



b)

Figure 4 Chemical composition of ZnO coatings produced by the HiPIMS (a) and RF (b) method.

The tests performed showed that the tested materials have very similar adhesion. The Fc3 parameter, defining the value of the indenter load at which the coating is removed from the entire scratch surface, was similar for both coatings and was for Fc3-ZnO_{HiPIMS}=39N and Fc3-ZnO_{RF}=40N, respectively. In both cases, the first form of damage in the crack area was adhesive damage Fc2 (Fc2-ZnO_{HiPIMS}=7N and Fc2-ZnO_{RF}=8N). On this basis, it should be assumed that for both coatings the fracture toughness in the scratch test is at least equal to the adhesion loss resistance (Fc1 ≥ Fc2). Analysis of the acoustic signal (AE) emitted from the damaged coating and SEM observations of coating damage occurring in the scratch area showed a significantly smaller amount of chips generated within the scratch area of the ZnO_{HiPIMS} coating (**Figure 4a**), which corresponds to the results of its high resistance to external loads connected with the H/E and H3/E2 ratios.

3. CONCLUSION

In this paper, thin films of ZnO deposited by both RF and HiPIMS magnetron sputtering have been compared in structural and mechanical properties. Both the HiPIMS and RF depositions were compared across average deposition power of 250 W. It was found that the depositions using different method (HIPIMS and RF) produced very similar results in deposition rate, morphology and adhesion of the coatings. It is worth noting that in several parameters, the HIPIMS deposition outperformed the RF process, possessing a higher ratio of hardness to elastic modulus (H/E) and higher plastic deformation H3/E2 coefficient. High plasticity index H3/E2 values can be beneficial in enhancing resistance to crack initiation and they can be beneficial for fracture toughness of the coating. SEM observations in the scratch test showed a significantly smaller number of chips formed within the scratch, which also confirms better resistance to cracking of the coating produced using HIPIMS. HIPIMS technology enables obtaining high power density, high ionization and high plasma density in the coating deposition process, which directly improves the mechanical properties of oxide coatings produced by this method.

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