Physico-Chemical and Mechanical Properties of DC-Sputtered ZrO_2 Coatings Prepared by Oblique Angle Deposition

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Abstract- In this study, a ZrO_2 thin film was deposited onto a Ti6Al4V substrate using the Oblique Angle Deposition (OAD) technique. The influence of the substrate/Zr target angle (15°, 30°, 45°, and 60°) was investigated, with a fixed azimuthal orientation (Phi) of 180°. The primary objective of this work is to develop and characterize novel biocompatible coatings for hip prosthesis implants with a complex 3D spherical geometry. The OAD method enables thin film deposition on such geometries and enhances understanding of how the particle incidence angle affects the surface morphology and microstructure of zirconium oxide (ZrO_2) thin films. This study combines an experimental approach DC magnetron sputtering with a multi-scale numerical approach using Monte Carlo codes (SRIM, SIMTRA, and NASCAM). The structure, texture, and growth of the ZrO_2 coatings were analyzed via X-ray diffraction (XRD), while microstructure and surface morphology were examined using scanning electron microscopy (SEM). Hardness and Young's modulus were determined through nanoindentation testing. Results indicate that increasing the oblique angle leads to a decrease in hardness. Experimental and numerical findings complement each other, offering deeper insight into the deposition phenomena. SIMTRA simulations closely replicate experimental observations: a higher number of incident particles results in increased coating thickness. Additionally, the film thickness decreases with increasing substrate inclination angle. The microstructure of ZrO_2 thin films is strongly influenced by substrate orientation, and coated substrates demonstrate superior performance compared to their uncoated counterparts.

Keywords: ZrO_2 coatings, OAD, Microstructure, Simulation, Mechanical Properties.

1. Introduction

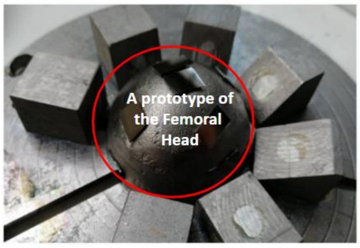
The hip joints are the largest synovial joints in the human body. They are composed of meniscal cartilage, which functions as a shock absorber. Damage to this cartilage can lead to mechanical pathologies of the hip, such as osteoarthritis and fractures. The primary treatment for end-stage hip degeneration is total hip arthroplasty (THA). The first THA was performed by Philip Wiles in 1938 [1], using a metal-on-metal bearing. Subsequent developments in prosthetic design led McKee et al. [2] to demonstrate that successful outcomes are achieved by resurfacing metal bearings with polyethylene. In addition, thin film coatings can further enhance implant performance. For example, TiN-coated implants reduce wear on both polyethylene and metal components compared to other materials used in prosthetics [3]. Tantalum (Ta) is also employed as a biomaterial due to its excellent biocompatibility and remarkable bioactive properties, as demonstrated in both in vitro and in vivo studies, particularly at the bone interface [4, 5]. Furthermore, ZrN/Zr/a-C multilayer thin films have shown outstanding performance, including low residual stress, high corrosion resistance, and favorable bio-tribological properties, making them suitable for protecting Ti6Al4V alloys. Haiyang et al. [6] investigated TiO_2, Ta_2O_5, and Nb_2O_5 coatings deposited on Ti6Al4V alloy substrates using radiofrequency spraying for potential medical applications. Their results indicated that all coatings improved the wear resistance, corrosion resistance, and biocompatibility of the Ti6Al4V surface. Rahmouni et al. [7] deposited nanostructured columnar zirconium (Zr) thin films on Ti6Al4V and CoCrMo substrates materials widely used in total joint replacements (TJRs) for hips and knees using DC oblique angle deposition (OAD) magnetron sputtering. Their findings revealed that Zr columnar thin films represent a promising approach for biomedical applications, including implants, due to their superior resistance to surface corrosion in physiological environments, provided the microstructure is finely controlled. The increase in joint arthroplasties and the growing number of highly active patients has led to progressive improvements in bearing surfaces. Although several materials are used and are among the most wear-resistant, better control of implant design is necessary to optimize their performance and durability [8]. However, to increase the lifespan of implants, the coating must exhibit strong adhesion, resistance to wear, plastic and elastic deformation, and biocompatibility. Zirconium (Zr) is one of the most promising candidates due to its excellent biocompatibility and acceptable mechanical properties [9]. Zirconia-based ceramics (ZrO_2) possess the best mechanical properties in terms of fracture toughness and strength among all oxide ceramics [10, 11]. Moreover, ZrO_2 is less prone to bacterial adhesion and is associated with fewer peri-implant inflammatory complications [12].

The aim of this work is to improve the durability of hip prostheses, which requires the careful selection of suitable coating materials. In this study, ZrO_2 thin films were prepared by magnetron sputtering to model deposition on a hemispherical surface, representative of the femoral head in artificial hip joints. This geometry is relatively complex, as the samples are not uniformly positioned on the hemisphere relative to the target, resulting in variations in substrate angle. Consequently, both angular and positional variations are observed. To enable deposition on this complex shape, the Oblique Angle Deposition (OAD) technique was employed one of the most widely used methods in sputtering processes. This technique involves tilting the substrates at angles (θ) of 15°, 30°, 45°, and 60°, with a fixed azimuthal orientation (phi) of 180°. During deposition, a mixture of argon (Ar) and a reactive gas is introduced into the chamber [13].

This study integrates both experimental (DC magnetron sputtering) and simulation approaches using Monte Carlo codes SRIM [14] and SIMTRA [15]. The structure and texture of ZrO_2 coatings on silicon substrates were analyzed using X-ray diffraction (XRD). Microstructure and surface morphology were examined via scanning electron microscopy (SEM), while mechanical properties specifically hardness were assessed through nanoindentation tests on Ti6Al4V substrates.

2. Experimental procedures

The OAD technique is used to model the deposition of coatings on a complex shape (femoral head). The scientific challenge of this work is to model half of this geometry (Fig. 1), which involves inclining the substrates from 15° to 60° with an orientation of 180° (all substrates are directed outward).



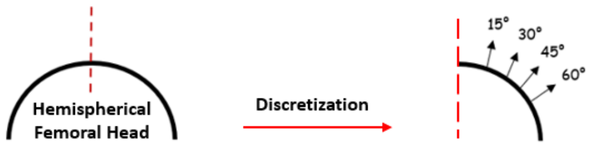


Fig. 1. The geometric configuration and prototype of the femoral head

This technique involves three key processes: the ejection of material from the target under ion bombardment, the transport of sputtered atoms to the substrate, and the subsequent growth of the film on the substrate (Fig. 2). The substrate holder accommodates four plates, each characterized by a different tilt angle θ (15°, 30°, 45°, and 60°) with a fixed orientation (phi) of 180°. After deposition, a thin layer is formed, consisting of well-structured columns. Each column is defined by an angle β, which is related to the direction of the particle flux. SIMTRA simulation is used to determine the flux incidence angle (α) and the number of particles deposited [15].

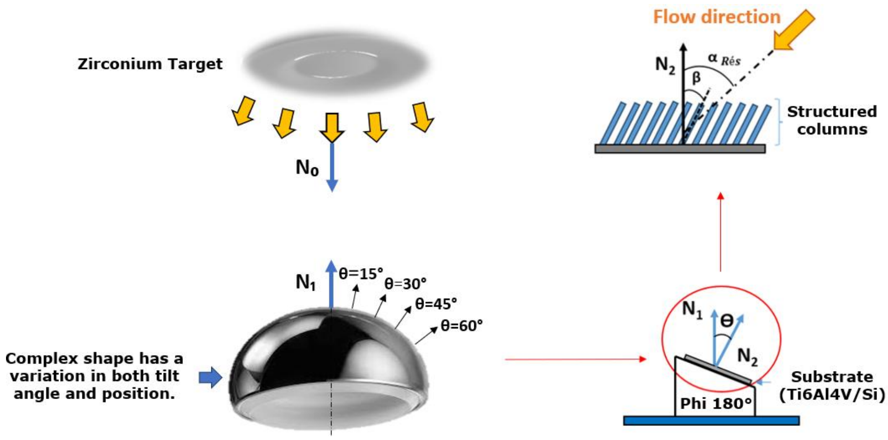


Fig. 2. Principle of the OAD technique

N_0, N_1, and N_2 are, respectively, the normal to the target, the normal to the substrate holder, and the normal to the substrate.

In this study, a 99.99% pure zirconium (Zr) disk (50 mm × 6 mm) was used as the target. The substrates included Si (100) silicon with a smooth micro-geometric surface (mirror-polished and defect-free), measuring 10 × 10 mm² and 0.38 mm thick, and Ti6Al4V (Grade 5), measuring 15 × 15 mm² with a thickness of 3 mm. The Ti6Al4V substrates were polished using SiC papers ranging from 180 to 2400 grit, followed by a final polish with 4000 grit to achieve a surface roughness (Ra) of 60 nm.

The coatings deposited on Si substrates were used to characterize microstructure, thickness, and surface morphology both in transverse section (column tilt angle) and top view using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). Coatings on Ti6Al4V substrates were used to investigate contact angle and to evaluate mechanical properties. Mechanical tests were performed using a Berkovich-type diamond indenter under a maximum normal load of 10 mN. For each ZrO_2 thin film, hardness was determined by averaging the results of ten indentations.

3. Results and Discussions

3.1 Morphology and microstructure of ZrO_2 films

The morphological structures of ZrO_2 at different tilt angles are illustrated in Fig. 3.

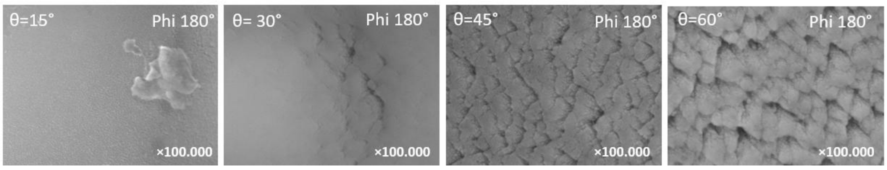


Fig. 3 SEM images of the surface morphology of ZrO_2 thin films sputtered by OAD at different inclination angles.

The substrate tilt angle influences the morphological structure of the ZrO_2 films. As shown in the top-view images in Fig. 3, the columns formed at lower tilt angles (15° and 30°) are small, compact, and homogeneous. At higher tilt angles (45° and 60°), the surface morphology changes noticeably, appearing studded with islands. A distinct columnar structure is observed, along with the emergence of spaces between columns, known as intercolumnar voids [16]. As the substrate tilt angle increases, the deposited films become progressively more porous. This phenomenon is attributed to the shading effect inherent to the OAD process [17]. Similar results have been reported for other oxides deposited using the GLAD technique, including Ta_2O_5 [16], Nb_2O_5 [18], ZnO [19], and TiO_2 [20].

Cross-sectional SEM images of ZrO_2 thin films, with substrates inclined at different tilt angles (θ), are shown in Fig. 4.

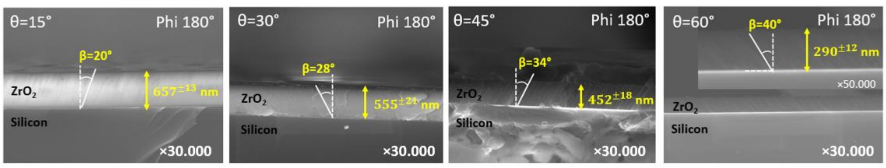


Fig.4 Cross-sectional images of the ZrO_2 thin films sputtered by OAD at different inclination angles.

All films exhibit a homogeneous columnar structure throughout their thickness, with columns tilted in the direction of the incident particle flux. Increasing the substrate tilt angle from θ = 15° to θ = 60°, with an orientation of phi = 180°, results in a corresponding increase in the column tilt angle (β) from 20° to 40°, and a reduction in film thickness from 657 nm to 290 nm (Fig. 4). This phenomenon is attributed to the shadowing effect and the limited diffusion of adatoms during the deposition process [15].

3.2 Thickness and number of particles

The thickness of ZrO_2 thin films was experimentally measured using cross-sectional SEM observations for each coating. Fig.5 presents the experimentally obtained film thickness as a function of the number of particles calculated using SIMTRA.

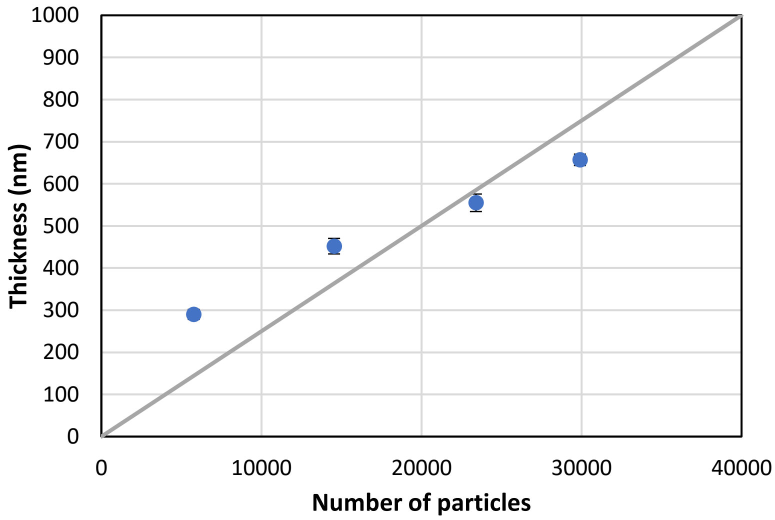


Fig. 5 Number of particles obtained with SIMTRA as a function of the experimentally measured film thickness.

The linear line represents perfect equality between the number of particles and the film thickness (x=y), serving as a reference. The layer thickness simulated using Simul3D software is determined based on the number of particles. However, this simulation does not take into account the crystallinity of the deposit or the material's intrinsic properties. In contrast, the number of atoms calculated with SIMTRA software corresponds only to the atoms arriving at the substrate surface.

A strong linear correlation is observed between the experimental thickness measurements and the values calculated using SIMTRA. The simulation results confirm the influence of atom transport from the target on the film thickness. As the number of particles increases, the film thickness increases accordingly, accurately reflecting the experimental observations.

3.3 Structural Properties

Fig. 6 illustrates the X-ray Diffraction (XRD) patterns of ZrO_2 thin films deposited by OAD on silicon substrates at tilt angles ranging from 15° to 60°, with a fixed orientation of phi = 180°.

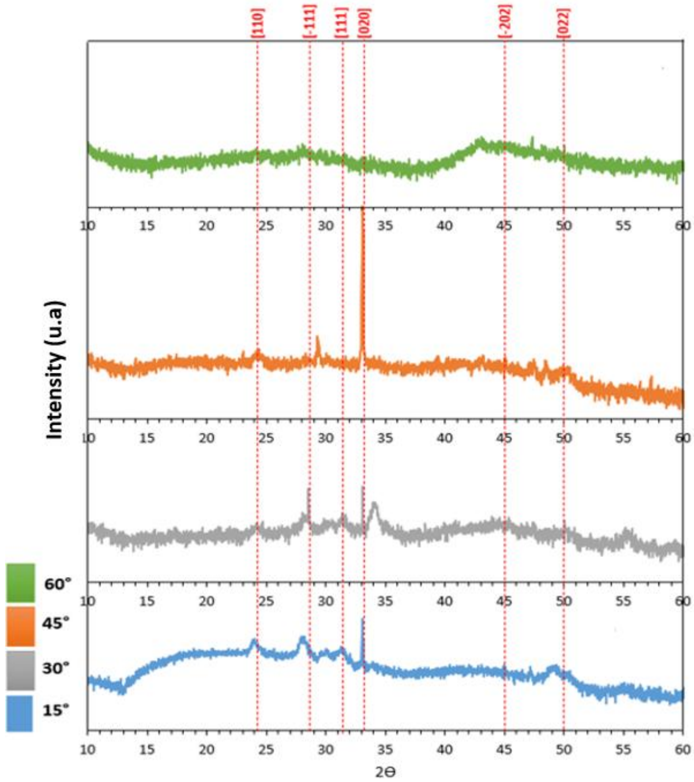


Fig. 6 XRD patterns of the ZrO_2 thin film deposited using the OAD technique

As observed, zirconium oxide films exhibit crystallinity at substrate tilt angles of 15°, 30°, and 45°. In contrast, the ZrO_2 coatings deposited at θ = 60° show no well-defined diffraction peaks, suggesting that these films possess an amorphous microstructure or that the crystallinity of the zirconium oxide layer is significantly reduced. This phenomenon can be attributed to the shadowing effect and the limited diffusion of adatoms during deposition [17]. The diffraction peaks at 24.2°, 28.2°, 31.4°, 33.2°, 45°, and 50° are assigned to the monoclinic ZrO_2 phase and correspond to the (110), (−111), (111), (020), (−202), and (022) planes, respectively [21, 22]. The dominant diffraction peak appears at 45°, indicating that the ZrO_2 films exhibit a preferred orientation along the (−202) plane

3.4 Mechanical properties

Fig. 7 illustrates the results of hardness and Young's modulus measurements obtained by nanoindentation.

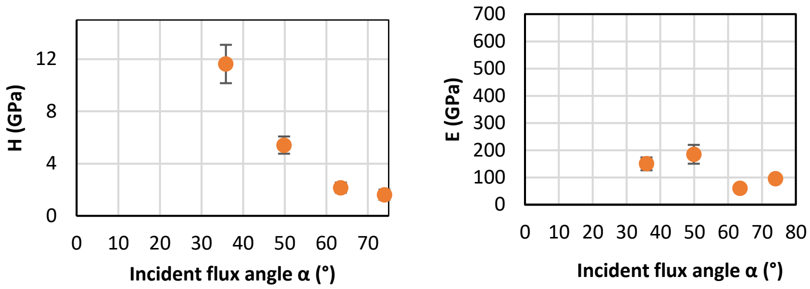


Fig. 7 Mechanical Properties of the ZrO_2 thin film deposited by OAD

Young's modulus (E) and hardness (H) decrease with increasing flux incidence angle (α), ranging from 36° to 74° (Fig. 7). Specifically, hardness decreases from 11.63 GPa to 1.62 GPa, while Young's modulus drops from 150 GPa to 95.61 GPa. This reduction in mechanical properties is primarily attributed to the increased porosity of the films [23]. At higher flux angles, the columns become more inclined and are increasingly separated by intercolumnar voids. These voids allow for relative movement and flexion between columns, which dissipates part of the applied mechanical energy. As a result, the shadowing effect becomes more pronounced, and the microstructure of the layers becomes progressively more porous [24]. It can be concluded that the mechanical properties of OAD-deposited ZrO_2 films are influenced by several factors including porosity, morphology, and structure with the flux incidence angle playing a particularly significant role.

4. Conclusion

This study investigates the growth behavior of ZrO_2 thin films deposited using the Oblique Angle Deposition (OAD) technique, with substrate inclination angles of θ = 15°, 30°, 45°, and 60°, and a fixed azimuthal orientation of Phi= 180°.
The key findings are summarized as follows:

- The structural and morphological properties of the films are strongly influenced by the substrate tilt angle.
- SIMTRA simulations confirm the impact of atomic transport from the target on film thickness.
- Simulated results show excellent agreement with experimental measurements.
- XRD analysis reveals that the main diffraction peaks correspond to the monoclinic phase of ZrO_2.
- The mechanical properties of OAD-deposited ZrO_2 films such as hardness and Young's modulus are governed by factors including porosity,

morphology, microstructure, and flux incidence angle. Notably, at α = 36°, the films exhibit optimal mechanical performance.

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