Applied Surface Science 258 (2012) 2612–2619

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

The role of target-to-substrate distance on the DC magnetron sputtered zirconia thin films' bioactivity

Arisara Thaveedeetrakul[a], Nirun Witit-anun[b,c], Virote Boonamnuayvitaya[a,*]

[a] Department of Chemical Engineering, King Mongkut's University of Technology Thonburi, Bangkok, Thailand
[b] Department of Physics, Burapha University, Chon Buri, Thailand
[c] Thailand Center of Excellence in Physics, CHE, Ministry of Education, Bangkok, Thailand

ARTICLE INFO

Article history:
Received 19 June 2011
Received in revised form 18 October 2011
Accepted 19 October 2011
Available online 25 October 2011

Keywords:
Zirconium dioxide
Magnetron sputtering
Simulated body fluid
Thin film
Hydroxyapatite

ABSTRACT

Zirconium dioxide thin films were deposited on 316L-stainless steel type substrates using DC unbalanced magnetron sputtering. The process parameter of this work was the target-to-substrate distance ($d_{t\text{-}s}$), which was varied from 60 to 120 mm. The crystal structure and surface topography of zirconium dioxide thin films were characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM). The results demonstrate that all of the ZrO_2 thin films are composed monoclinic phase. The film sputtered at short $d_{t\text{-}s}$ (60 mm) shows a rather heterogeneous, uneven surface. The grain size, roughness, and thickness of thin films were decreased by increasing $d_{t\text{-}s}$. The bioactivity was assessed by investigating the formation of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) on the thin film surface soaked in simulated body fluids (SBF) for 7 days. XRD and scanning electron microscopy (SEM) were used to verify the formation of apatite layers on the samples. Bone-like apatites were formed on the surface of the ZrO_2 thin film in SBF immersion experiments. A nanocrystalline hydroxyapatite (HA) with a particle size of 2–4 μm was deposited. Higher crystallinity of HA on the surface was observed when the distance $d_{t\text{-}s}$ increased to more than 80 mm. Therefore, it seems that a $d_{t\text{-}s}$ greater than 80 mm is an important sputtering condition for inducing HA on the zirconia film.

1. Introduction

Artificial materials to be used as substitutes for high load bearing bones, such as femoral head, knee joint, and tibia bones, need the ability to bond directly with bone and also high fracture toughness. The toughness of the bioactive ceramics is relatively weak compared with human cortical bone and common implant metal [1]. Meanwhile none of the metals bond directly to living bone, as a result bioceramic materials are often used as coating relying on the mechanical strength and toughness of the substrate [1–3]. The use of the bioceramic coating on a metal implant can lead to earlier stabilization of the implant in the surrounding bone and extend the functional life of the prosthesis [1].

Zirconium oxide or zirconia thin films (ZrO_2) have three crystal structures depending on temperature: monoclinic below 1170 °C, tetragonal between 1170 and 2370 °C, and cubic phase above 2370 °C [4]. Zirconia was considered an attractive ceramic for biomedical application due to its inertness, high strength, corrosion resistance, and fracture toughness. It undergoes little or no chemical change during long-term exposure to body fluids. Zirconia has been applied to orthopaedic uses such as hip and knee joints [5,6].

Several techniques have been used to produce zirconia coatings, including chemical vapour deposition (CVD) [7,8], sol–gel [3,9,10], ion beam deposition [11], plasma spraying [12,13], cathodic arc deposition [14], and sputtering [15–19]. There are disadvantages to some of the above techniques; for example the CVD and cathodic arc methods require high deposition temperatures, which lead to stresses in films deposited on materials with different thermal expansion coefficients, which can cause mechanical instabilities in the deposited films [20,21]. In the sol–gel method, the disadvantages are the health hazard presented by the organic solution residues and low adherence of the deposited films [21,22]. Similarly, the films synthesized by plasma spraying have low adherence to the substrate and poor crystallinity [23]. The limitation of ion beam deposition is that it is generally able to cover only rather small areas and has low deposition rates [21]. In contrast, it is found that the magnetron sputtering process is largely applied because of the good adherence and smoothness of obtained films at low deposition temperature [23–25]. However, this technique has not yet been well studied for the production of zirconia films with the purpose of the applications mentioned.

Tests in simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma have become a

* Corresponding author. Tel.: +66 2470 9221x222; fax: +66 2428 3534.
E-mail address: virote.boo@kmutt.ac.th (V. Boonamnuayvitaya).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.10.104

prerequisite to the prediction of *in vivo* behaviour of orthopaedic biomaterials. Kokubo and Takadama showed that zirconium hydrogel coating could induce bone-like apatite in SBF [26]. The apatite layers which formed on the substrates have identical properties to human bone, which is an essential requirement for implant materials. In addition, the report also indicated that pure zirconia gel induced the formation of apatite in SBF only when it possessed a tetragonal or a monoclinic structure [27].

In this work, zirconia films were deposited by dual cathode (DC) unbalanced magnetron sputtering. By strengthening the dual cathode magnetrons, ion bombardment at the substrate was increased with a consequent improvement in coating structure. The process parameter varied was the target-to-substrate distance ($d_{t\text{-}s}$). All samples were soaked in an SBF to verify the formation of hydroxyapatite on the zirconia film. Factors affecting the hydroxyapatite formation are discussed.

2. Material and methods

Zirconia thin films were deposited using DC unbalanced magnetron sputtering. A metallic zirconium target (54 mm in diameter and 99.7% pure, VT-SUN, Thailand) was used. In this work, the sputtering was carried out with two cathodes but only one cathode was used during deposition of the zirconia films. However, the magnetic field of the unused magnetron increases the plasma density and enhances the ionization of the sputtered Zr. Fig. 1 shows a schematic diagram of the sputtering apparatus used in this work. The substrate materials were Si (1 0 0) wafer and 316L stainless steel type (316L-SS, provided by Thainox Company, Thailand), 10 mm × 10 mm × 1 mm in size. All substrates were ultrasonically cleaned in acetone and propanol for 5 min each. Before sputtering, the vacuum chamber was evacuated to a base pressure lower than 5.0×10^{-5} mbar and pre-sputtered for 5 min to remove impurities from the target surface. The sputtering gases, Ar with a purity of 99.999% (TIG, Thailand) and reactive O_2 with a purity of 99.999% (TIG, Thailand), were introduced to the chamber separately and controlled by the mass flow controllers (MKS type 247D). The sputtering time was kept constant for 120 min with a discharge current of 500 mA in all experiments. All substrates were deposited with no external heating. The deposition conditions of the DC unbalanced magnetron sputtering are shown in Table 1.

Table 1
The deposition parameters for DC unbalanced magnetron sputtered ZrO_2 thin films.

Condition	Value
Ar:O_2 flow rate (sccm)	1:4
Base pressure (mbar)	5.0×10^{-5}
Sputtering gas pressure (mbar)	5.0×10^{-3}
Discharge current (mA)	500
Deposition voltage (V)	350–380
Target-to-substrate distance, $d_{t\text{-}s}$ (mm)	60, 80, 100, 120
Substrates	Si, 316L-SS

316L-SS type substrates coated with the zirconia films were washed with ultra-pure water and ethanol in ultrasonic bath for 10 min before soaking in 30 ml of an acellular SBF having the same ion concentrations as human plasma (142.0 mM Na^+, 5.0 mM K^+, 2.5 mM Ca^{2+}, 1.5 mM Mg^{2+}, 148.8 mM Cl^-, 4.2 mM HCO^{3-}, 1.0 mM $HPO_4{}^{2-}$, and 0.5 mM $SO_4{}^{2-}$) [26] at 37 °C. The SBF solution was prepared by dissolving high-purity chemical reagents, NaCl (Merck, Germany), $NaHCO_3$ (Ajax Finechem), KCl (RFCL Limited.), $K_2HPO_4{\cdot}3H_2O$ (Carlo Erba), $MgCl_2{\cdot}6H_2O$ (Ajax Finechem), HCl (Mallinckrodt Chemical), $CaCl_2$ (Ajax Finechem), and Na_2SO_4 (Ajax Finechem), in ultra-pure water and buffering at a pH of 7.40 at 37 °C using tris(hydroxymethyl)-aminomethane ($(CH_2OH)_3CNH_2$) (Ajax Finechem) and HCl. All chemicals were high purity reagents and were used without further purification. The SBF solution was not renewed during the experiment. After 7 days, the samples were removed from the solution, gently washed in ultra-pure water, and dried at room temperature. The two samples were tested in SBF for each deposition condition.

The crystal structures of samples were examined using an X-ray diffractometer with a thin-film mode (TF-XRD, RINT-2100, Rigaku) at a grazing incidence diffraction of 3°. The X-ray source was copper Kα radiation with a wavelength of 1.54 Å. The measured 2θ angles

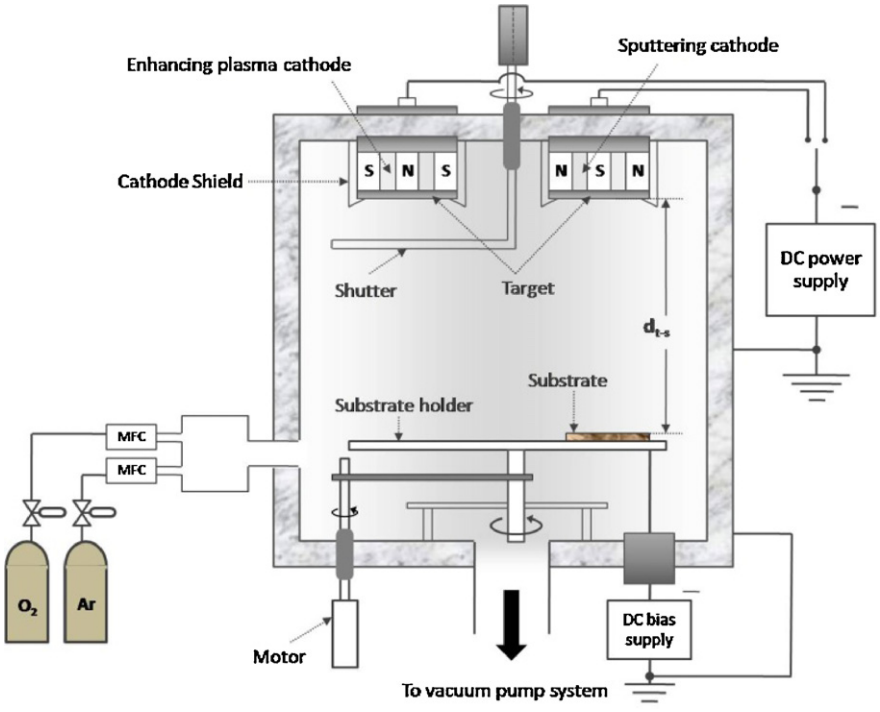

Fig. 1. Dual cathode DC unbalanced magnetron sputtering diagram.