

# Apatite Deposition on ZrO<sub>2</sub> Thin Films by DC Unbalanced Magnetron Sputtering

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## ABSTRACT

Zirconia thin films deposited on 316L stainless-steel substrate were prepared by DC unbalanced magnetron sputtering from a metallic zirconium target at low temperature with the target-to-substrate distance ( $d_{t-s}$ ) of 100 mm and sputtering power of 180 W. High purity gas of Ar as the working gas and O<sub>2</sub> as the reactive gas were used. The depositions were performed for 120 min at a total pressure of 0.5 Pa. The effect of thermal treatment on the HA formation was investigated. The bioactivity was assessed by investigating the formation of hydroxyapatite (HA) on the surface soaked in simulated body fluids (SBF). Films structure, surface morphology and chemical composition of the ZrO<sub>2</sub> films and HA formation were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and FT-IR spectroscopy. The XRD results demonstrate the ZrO<sub>2</sub> films are monoclinic phase. The annealed films show the higher film crystalline due to the rearrangement of film structure. After being immersed the samples in SBF, the bone-like apatite was observed on all ZrO<sub>2</sub> films, but a denser and more continuous HA layer were observed on annealed films due to the crystallinity of ZrO<sub>2</sub> films.

**Keywords:** Component; Zirconium Dioxide; Magnetron Sputtering; Hydroxyapatite; Simulated Body Fluid

## 1. Introduction

Thin films of zirconium dioxide (ZrO<sub>2</sub>) or zirconia are widely used in protective and thermal barrier coatings [1], optical filter [2], oxygen sensor, microelectronic devices and biocompatibility of bone implants [3-5]. It was considered an attractive ceramic for biomedical application due to its inertness, high strength, corrosion resistance, and fracture toughness. The ZrO<sub>2</sub> have three crystalline polymorphs, namely: monoclinic, tetragonal and cubic [6]. Both the monoclinic and tetragonal phases exhibit excellent biocompatibility properties on their surfaces [7].

Bioactivity is widely accepted as the essential requirement for an artificial to exhibit chemical bonding to living tissues upon the formation of a bone-like apatite layer on its surface in any simulated body environment [8].

The formation of a bone-like apatite layer on biomaterials is assumed to be the precondition for their osteoinductivity to induce bone formation on the biomaterials in non-osseous site. The research method of bone-like apatite formation *in vitro* commonly is to immerse specimen in simulated body fluid (SBF) and hydroxyapatite (HA) layer can be formed on all kinds of bioactive materials [9]. The *in vitro* tests of zirconium hydrogel coating have found new bone-like apatite layer formation on the surface [7]. Clinical studies of ZrO<sub>2</sub> thin films are now expected to be the useful as bone substitutes even under highly loaded conditions such as is found in femoral and knee joint since they exhibit high fracture toughness as well as high bond-bonding ability [10].

There are many methods to prepare the ZrO<sub>2</sub> thin films., however, the sputtering technique is a very attractive process

for producing metallic oxide with good uniformity at low temperature [11]. This technique has not yet been well studied for the deposition of ZrO<sub>2</sub> films with the purpose of the applications mentioned.

In this study, the ZrO<sub>2</sub> thin films were deposited by DC unbalanced magnetron sputtering technique followed by the thermal treatments. All samples were immersed in a SBF solution for demonstration the bone-like apatite on the ZrO<sub>2</sub> films. The effect of the pretreatment on the formation of the HA was investigated.

## 2. Experimental

Reactive magnetron sputtering, with zirconium target of 54 mm diameter, was used to produce the ZrO<sub>2</sub> thin films with the sputtering power of 180 W. The coatings were deposited on 316L-stainless steel type substrate, 10 mm × 10 mm × 1 mm in size. The chemical pretreatment of the substrates was carried out by cleansing with propanol and acetone in ultrasonic bath for 15 min. The sputtering gases argon with a purity of 99.999% and reactive oxygen with a purity 99.999% of which flow rates of 1 and 4 sccm, respectively, were introduced to the chamber separately and controlled by the mass flow controllers (MKS type 247D). The target was sputter cleaned for 15 min at the argon pressure lower than 0.005 Pa to remove impurities from target surface. The  $d_{t-s}$  was adjusted to 100 mm and the base pressure of the system was 0.005 Pa. The depositions were performed for 120 min at a total pressure of 0.5 Pa. Some as-deposited ZrO<sub>2</sub> films were annealed in air at the temperature of 800 °C for 1 h.

The SBF solution that had ionic concentration close to human blood plasma, as shown in **Table 1**, was prepared by dissolving reagent-grade NaCl, NaHCO<sub>3</sub>, KCl, K<sub>2</sub>HPO<sub>4</sub>•3H<sub>2</sub>O, MgCl<sub>2</sub>•6H<sub>2</sub>O, CaCl<sub>2</sub>, and Na<sub>2</sub>SO<sub>4</sub> in ultra-pure water. The solution was buffered at pH of 7.4 with 1M HCl and tris (hydroxymethyl) aminomethane ((CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>2</sub>) at 37C. The samples were immersed into solution at 37C for 7 days. Subsequent to immersion, the samples were removed from the solution, gently rinsed with the ultra-pure water, and then dried at room temperature.

The surfaces of the substrates before and after immersion of SBF solution were analyzed via X-ray diffractometer with a thin-film mode (TF-XRD) adjusted with CuK $\alpha$  radiation. The measured 2 $\theta$  angles were recorded from 20 to 40° at a step rate 1°min<sup>-1</sup>. The morphology of the SBF-immersed samples was observed by the scanning electron microscopy (SEM). FT-IR spectroscopy was measured in transmission using the KBr pellet technique.

### 3. Result and Discussion

#### 3.1. Deposition of Monoclinic ZrO<sub>2</sub> and Further Annealing

It is well known that the sputtered films have lower packing density and annealing improved the packing density and improved crystallinity. X-ray diffraction patterns of the as-deposited and annealed films are shown in **Figure 1**. The results also reveal that the as-deposited films are crystalline in nature. The monoclinic phase was formed without any phase mixing (JCPDS file no. 89-9066). The as-deposited and annealed films in **Figure 1** were characterized by three broad peaks with locating at 2 $\theta$   $\approx$  28.2°, 34.1°, and 35.3°, indicating the films contain monoclinic phase with the M(111), (002) and (200) orientations, respectively. The existence of pure monoclinic phase at high temperatures observed in the present work is similar to that noticed by Venkataraj et al. [12]. In addition, the ZrO<sub>2</sub> thin film with heat treatment in **Figure 1(a)** shows a narrower peak with higher intensity, implying a higher crystallinity, compared with the as-deposited film (**Figure 1(b)**). These results reveal that the quality of ZrO<sub>2</sub> film was improved after annealing. These data indicate significant migration of atoms and thus changes in film atomic structures at high temperatures.

The mean crystalline size in the ZrO<sub>2</sub> films is determined using the well-known Scherrer equation [13] on the basis of ZrO<sub>2</sub> peak with higher intensity as shown in **Table 2**. The crystal size calculated from the (111) peak of the annealed film is larger than the as-deposited films due to the increase of the atom and

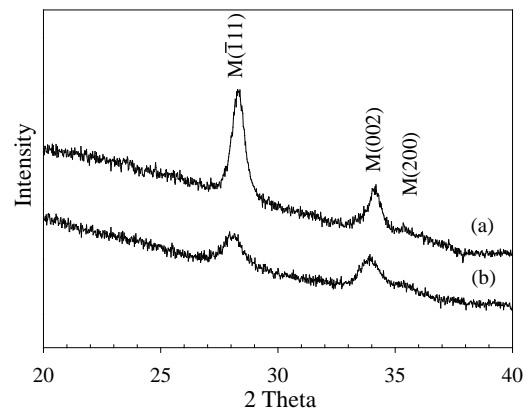
**Table 1. Ionic concentrations of SBF in comparison with those of human blood plasma.**

Concentration (mM)	Blood Plasma	SBF
Na <sup>+</sup>	142.0	142.0
K <sup>+</sup>	5.0	5.0
Ca <sup>2+</sup>	2.5	2.5
Mg <sup>2+</sup>	1.5	1.5
HCO <sub>3</sub> <sup>-</sup>	27.0	4.2
Cl <sup>-</sup>	103.0	147.8
HPO <sub>4</sub> <sup>2-</sup>	1.0	1.0
SO <sub>4</sub> <sup>2-</sup>	0.5	0.5

grain boundary mobility in the film [14]. These results reveal that the quality of ZrO<sub>2</sub> film was improved after annealing.

#### 3.2. HA Formation on As-Deposited and Annealing ZrO<sub>2</sub> Films

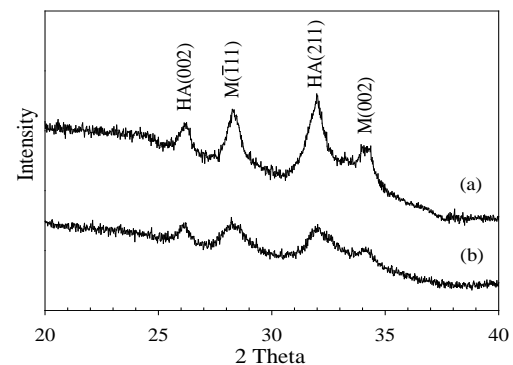
The bioactivity of the ZrO<sub>2</sub> films was assessed by SBF immersion tests. The samples after incubation in SBF for 7 days were analyzed by XRD to determine the crystal structure of the newly formed layers. **Figure 2** shows the formation of HA peaks as well as the monoclinic ZrO<sub>2</sub> peaks for both as-deposited and annealed samples. Two new diffraction peaks at about 25.9° and 31.8° can be referred to crystalline apatite according to JCPDS file no. 09-0432. The low intensity and broad peak indicate that the amount of as-grown crystalline apatite on the ZrO<sub>2</sub> thin film is small and the crystallinity is low. When the sample was annealed at 800C, the HA peak became more intense and shaper (**Figure 2(a)**). This may ascribe to dense of HA formation or high crystallinity of HA.



**Figure 1. XRD patterns of the ZrO<sub>2</sub> thin films deposited on 316L-SS type substrates: (a) annealing at 800°C and (b) as-deposited.**

**Table 2. FWHM and crystal size of zirconia thin films M(111).**

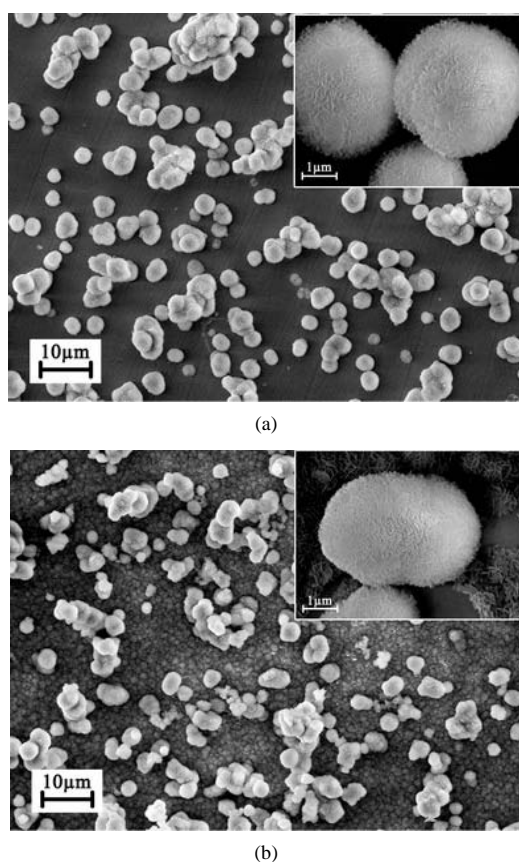
Sample	FWHM (degrees)	Crystal size (nm)
as-deposited	0.90	18.45
800°C	0.59	28.16



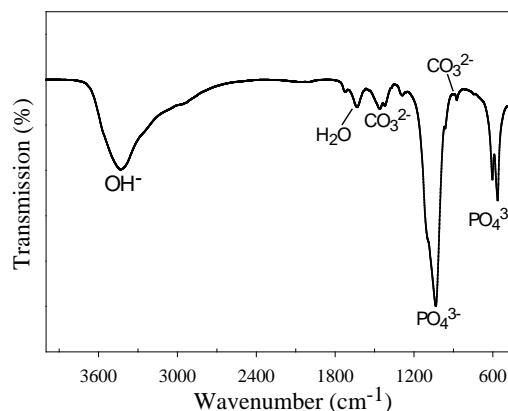
**Figure 2. XRD patterns for the ZrO<sub>2</sub> samples tested in SBF for 7 days: (a) annealing at 800°C and (b) as-deposited.**

The calcium and phosphate ions required for hydroxyapatite generation on the film surface were derived from the SBF. The result obtained from the present study indicates that Zr-OH groups, abundant on the surface of the thin film, are able to induce apatite nucleation in a similar manner as Si-OH, Ti-OH, and Ta-OH group do. Nevertheless, Uchida et al. [7] found the apatite-forming ability of the gels with tetragonal or monoclinic structure was apparently much higher than that of the gel with amorphous structure. This implies that not all types of Zr-OH groups, but only Zr-OH group with specific arrangements based on tetragonal or monoclinic structure, are effective in inducing apatite nucleation.

The microstructures of the as-deposited and annealed ZrO<sub>2</sub> films after soaked in SBF for 7 days were observed by SEM as shown in **Figure 3**. Both the samples can induce hydroxyapatite form on the films surface. The HA particles was island-like and spherically shaped with diameter size about 2 to 3 μm. For the as-deposited sample (**Figure 3(a)**), only a small amount of HA particles formed sparsely scattered on the surface of the sample. The morphology is very similar to that of the deposited apatite on the surface of zirconia gel through biomimetic processing utilizing SBF [7]. However, a denser and more continuous HA layer was observed on annealed films (**Figure 3(b)**). The small HA particle size under the aggregation is about 600 nm in diameter. These results indicate that the annealed ZrO<sub>2</sub> films with a high crystallinity are more bioactive compared with low crystallized structure.



**Figure 3.** SEM micrographs of HA formation after soaking in SBF solution for 7 days: (a) as-deposited and (b) annealing at 800°C.



**Figure 4.** FT-IR spectra of HA formed on the samples in SBF for 7 days.

In order to confirm the structure of the Ca-P layer, we performed FTIR analysis, as shown in **Figure 4**. The phosphate group itself has a tetrahedral symmetry; resulting in four vibrational modes (symmetric stretch ( $\nu_1$ ) at 958 cm<sup>-1</sup>; asymmetric stretch ( $\nu_2$ ) at 430 - 460 cm<sup>-1</sup>; ( $\nu_3$ ) at 1041-1090 cm<sup>-1</sup>; ( $\nu_4$ ) at 575 - 610 cm<sup>-1</sup>) [15]. An OH<sup>-</sup> absorption peak at 3440 cm<sup>-1</sup> can be seen in the spectra. The absorption peak at 1635 cm<sup>-1</sup> can be assigned to absorbed H<sub>2</sub>O groups, which is a common characteristic of precipitates in aqueous solutions [16]. Furthermore, peaks between 1400 - 1450 cm<sup>-1</sup> are due to the C-O stretching of CO<sub>3</sub><sup>2-</sup> groups, which indicate that the apatites formed on the ZrO<sub>2</sub> thin films are bone-like carbonate-containing apatite [16].

#### 4. Conclusion

Zirconium dioxide thin films of monoclinic phase have been deposited by DC unbalanced magnetron sputtering and the film was subjected to thermal treatment. The annealed films show the higher film crystalline due to the rearrangement of film structure. After being immersed the samples in SBF, the bone-like apatite was observed on all ZrO<sub>2</sub> films, but a denser and more continuous HA layer was observed on annealed films due to the crystallinity of ZrO<sub>2</sub> films. These results show that the sputtered ZrO<sub>2</sub> thin films exhibit good bioactivity.

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