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Multilayer zirconium titanate thin films prepared by a sol–gel deposition method

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Abstract

Zirconium titanate multilayer thin films were prepared by an aqueous particulate sol–gel process followed by spin coating. The obtained structures were studied by transmission electron microscope, scanning electron microscope, atomic force microscope, and spectroscopic reflection analyses. According to the results, sound thin films up to three layers were developed, accompanied by an increase in thickness and roughness by increasing the number of the layers. It was also found that the coatings consist of globular nanoparticles

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with an average diameter of 50 nm. Considering the contribution of roughness to biological responses, the optimization of the surface characteristics to meet an optimal performance seems to be a challenging issue, which demands future studies.

Keywords: Films (A); Sol–gel processes (A); Electron microscopy (B); Microstructure-final (B)

1. Introduction

Zirconium titanate ($ZrTiO_4$), with the orthorhombic α-PbO_2 type structure in powder, fiber, coating, and bulk forms, is a ceramic considered in electronic, optical, chemical, catalytic, and biomedical purposes [1-6]. Typically, $ZrTiO_4$ thin films and coatings have attracted much attention especially in dielectric applications demanding a high resistivity and dielectric constant [7] and more recently in biomedical applications requiring biocompatibility and bioactivity [6,8]. To process thin films and coatings, among various methods used, the sol–gel deposition process has advantages such as high homogeneity (as mixing occurs on the atomic level), low sintering temperatures (due to small particle sizes), and simplicity of complex shape coating [9,10].

Although widespread studies have been conducted on lead zirconate titanate (PZT), titania (TiO_2), and zirconia (ZrO_2) films, little systematic work has been reported on $ZrTiO_4$ coatings and thin films, especially those considered in biomedical fields and those prepared by the sol–gel route. Referring to the literature, for instance, physical, mechanical, and tribological characteristics of $ZrTiO_4$ coatings prepared by magnetron sputtering for orthopedic and dental implants have been reported [6]. In addition, the thickness dependency of dielectric properties of $ZrTiO_4$ thin films developed by a surface sol–gel process using butoxides as the precursor has been studied [11]. Devi et al. [8] have also investigated the

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structure and bioactivity of $ZrTiO_4$ coated on a biomedical stainless steel by a non-hydrolytic sol–gel method starting from titanium tetraisopropoxide and zirconium oxychloride. However, facile, inexpensive, and high-quality processing of materials is an essential concern from both the scientific and technological viewpoints. Recently, an aqueous particulate sol–gel method using chlorides as the precursor was successfully experimented to synthesize $ZrTiO_4$ nanoparticles [12]. Compared to polymeric sol–gel methods, the typical advantage of this facile route is employing chlorides rather than alkoxides as the precursor to develop a product at lower cost. In this paper, the structure of multilayer thin films obtained from the aforementioned particulate sol–gel method followed by spin coating is characterized by transmission electron microscopy, field emission scanning electron microscopy, atomic force microscopy, and spectroscopic reflection. Additionally, a natural polymer, namely carboxymethyl cellulose was used to improve the dispersion of the synthesized nanoparticles in the aqueous sol.

2. Experimental procedures

Initially, 9.1 mmol of zirconium tetrachloride ($ZrCl_4$, Alfa Aesar, 99.5 %) and titanium tetrachloride ($TiCl_4$, Alfa Aesar, 99.99 %) were added to 200 mL of deionized water and magnetically stirred for 2 h. Afterwards, the pH value of the solution was enhanced to 7 by adding a 2 M NaOH solution dropwise. The hydrogel was rinsed several times with deionized water to remove chloride ion and centrifuged at 6000 rpm for 10 min. To prepare a sol of appropriate viscosity for spin coating, 75 mL of deionized water and 2 wt.% carboxymethyl cellulose (CMC, sodium salt, Alfa Aesar) were added, followed by sonication for 1 h. CMC was used as a dispersing agent to improve the dispersion of nanoparticles in the aqueous sol. The resultant sol viscosity was 80 mPa.S, measured using a Bohlin C-VOR rheometer.

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Austenitic stainless steel substrates were ground by No. 180-3000 emery papers gradually and mirror polished with 1 and 0.1 μm alumina powders. They were then ultrasonically cleaned in acetone, ethanol, and distilled water respectively, followed by spin coating with the above sol at 3000 rpm for 60 sec. The wet coated samples were immediately dried at 80 °C for 1 h in an oven. The further heat treatment was conducted under a nitrogen atmosphere at a rate of 5 °C/min by heating to 200 °C, holding for 15 min, heating to 400 °C, holding for 15 min, heating to 700 °C, and holding for 1 h. This thermal cycle was designed based on the material's thermal behavior to conduct the gradual removal of residual volatile materials and to prepare sound films, where the material presents a sharp weight loss when heating from 100 °C to 400 °C [12]. The above processes including deposition, drying, and sintering were repeated three times to prepare mono, double, and triple-layer films.

The film surfaces were studied by a field emission scanning electron microscope (SEM, Hitachi S-4800) and Veeco Multimode atomic force microscope (AFM, (Bruker AXS) to evaluate the film quality and roughness. The film thickness was also measured by a NanoSpec 3000 system (Nanometrics, CA, USA) utilizing a modern small spot spectroscopic reflectometer. A transmission electron microscope (TEM, JEOL JEM-2100) operating at an acceleration voltage of 200 kV was also used to evaluate the powder particle size and morphology.

3. Results and discussion

The maximum sound film thickness obtained in one deposition step, which is limited initially by agglomeration on the substrate rather than a desirable coverage and then cracking during firing, was determined by varying the amount of deionized water used in the sol for the same spin coating condition. When viscosity is increased by decreasing the water content

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to less than that used in this work (75 ml for 9.1 mmol of $ZrCl_4$ and $TiCl_4$ with a viscosity of 80 mPa.S), the sol does not cover the surface uniformly and tends to form droplets instead of a liquid film, which causes non-uniform films. Apart from this limitation, thicker films are more prone to cracking, due to the removal of a higher amount of volatile materials and more shrinkage during firing. However, to obtain thicker films, multilayer processing to 3 steps was employed. It is clear that the surface performance of metal oxide thin films depends on their morphological features. To do so, SEM and AFM analyses were done to evaluate the film morphology and roughness.

Fig. 1 demonstrates the SEM micrograph of the single, double, and triple-layer films with the CMC addition, in which the development of relatively dense, smooth, well-covering, uniform and crack-free coatings is evident. The desirable characteristics of the films are attributed to the presence of CMC in the sol and the merit of the deposition and firing processes allowing the gradual removal of volatile materials (residual water and chloride) from the prepared films which are thin enough. Successfully, CMC as the dispersing agent makes the ceramic nanoparticles be negatively charged and depresses their hydrophobicity and agglomeration. Based on the steric stabilization theory [13-16], a strong steric repulsion between these particles is created, leading to a high stability of the colloidal dispersion and uniform dispersion of the ceramic particles in the aqueous sol. This is an essential requirement to obtain defect-free coatings during sol–gel processes. On the other hand, a slight decrease of flatness is observed by increasing the number of the layers, as will be detailed by the AFM studies.

The film thickness measured by the spectroscopic reflectometer is illustrated in Fig. 2(a), which clearly signifies an enhancement in thickness by increasing the number of the layers. It can be also realized that the thickness of the individual layer is not similar, where it

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might be expected that the thickness of the double and triple-layer thin films is almost two and three times of the monolayer film respectively. It is due to the fact that some nanoparticles which are spin-coated on the previously coated substrate tend to deposit on pores and defects of the previous layer, providing denser coatings. In contrast, Seveno et al. [17] have pointed out that the thickness of $PbZr_{0.45}Ti_{0.55}O_3$ ferroelectric films prepared by a polymeric sol–gel method follows a linear trend as a function of the number of deposition layers, i.e. the thickness of the individual layers is almost the same. This discrepancy can be explained by considering the different natures of the sol–gel routes applied, where particulate sol–gel processes generally provide larger pores compared with polymeric sol–gel routes. Indeed, in our case, the particle size is very smaller than the surface roughness and valleys; hence, the particles effectively cover surface defects and valleys. It is also noteworthy that the used sol includes nanoparticles of 5 nm in size [12].

Fig. 3 indicates the three dimensional AFM images of the single, double, and triple-layer $ZrTiO_4$ films, suggesting smooth, uniform, and dense films, as confirmed by SEM. AFM also allows determining the surface roughness value by considering the distribution curve of relative height among points in the scanning area and calculating the average value with respect to a central plane. The average roughness value of the single, double, and triple-layer films over areas of 5×5 μm^2 is presented in Fig. 2(b), extracted from the AFM analyses using the DI NanoScope 7.20 software. It can be seen that by increasing the number of the layers, the roughness is increased slightly, despite the fact that pores and defects of the previous layer are covered by the subsequent layer (as explained for the thickness evolution). The grown multilayer thin films before annealing are found to have a smooth surface with a roughness less than 4 nm. During sintering the nanoparticles grow, as shown in Ref. [12], and start appearing on the surface due to a mass transfer caused by transformation from a glass

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state to a crystalline one [18]. Indeed, initially a strained continuous layer is formed on the substrate and then the strain is released by the formation of three-dimensional islands on that layer (Stranski–Krastanov growth model) [19,20], thereby providing rough films with a large number of valleys and mountains. Afterwards, the next deposited layer before sintering would smooth the surface and create a roughness value as small as 4 nm. But due to sintering of the newly deposited layer, if new islands are formed through valleys of the previous film or shrinkage in the valleys is less than mountains, roughness would decrease. In this study, the increase in the roughness value of the films by increasing the number of the layers suggests that this circumstance does not govern. On the other hand, it has been reported that residual stresses in the previous layers constrict the final layer and avoid the uniform coverage of the surface, increasing roughness [21]. At a higher magnification, the two- and three-dimensional AFM images (Fig. 4) show that the coating consists of globular nanoparticles with 15 nm to 130 nm in size and an average diameter of 50 nm, which is in agreement with the TEM micrograph of the calcined sample provided in Fig. 5. The high crystallinity of this sample results in distinct Debye-Scherrer diffraction spots in the corresponding selected area diffraction (SAD) pattern [Fig. 5(b)], which is reasonable by considering the fact that the crystallization temperature of the material is about 690 °C [12].

This type of crack-free and uniform coatings can be regarded in different applications dealing with either stainless steels or zirconium titanate as the functional component. For example in biomedical applications, these coatings not only can protect the surface of metallic implants like stainless steels against wear and corrosion, but also affect hydrophilicity, biocompatibility, and bioactivity. Typically, the effect of thickness and roughness on the aforementioned properties seems to be an interesting subject, where there are antitheses, for instant, on the effect of roughness on bioactivity and cell adhesion. In this

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regard, Hong et al. [22] reported that rough surfaces provide a higher cell adhesion compared to microscopically smooth surfaces since the more surface area induces the more reactivity of cells and surface. Nonetheless, Bigerelle et al. [23] showed that when roughness is less than the cell scale (micron), isotropic smooth surfaces are preferred from the cell adhesion viewpoint. On the contrary, in the case of roughness higher than the cell scale, cells take advantage of isotropic rough surfaces. Since the roughness values of the coating developed in this work are less than the cell scale, probably smoother surfaces present a better cell adhesion. On the other hand, rougher surfaces having higher surface areas generally represent better bioactivity [24,25]. Certainly, a precise conclusion on the related issues (biological response) demands further studies in the future.

4. Conclusions

Multilayer thin films prepared by an aqueous particulate sol–gel method using CMC as the dispersant were focused. From this work, the following conclusions could be drawn:

- The development of well-covering, crack-free, and homogeneous $ZrTiO_4$ thin films was confirmed by SEM and AFM, suggesting the merit of processing.
- A non-linear increase in the thickness and roughness of the multilayer films was found by increasing the number of the layers up to three, realized by the spectroscopic reflectometer and AFM.
- The films contained globular nanoparticles with an average diameter of 50 nm, based on AFM and TEM.

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Figures

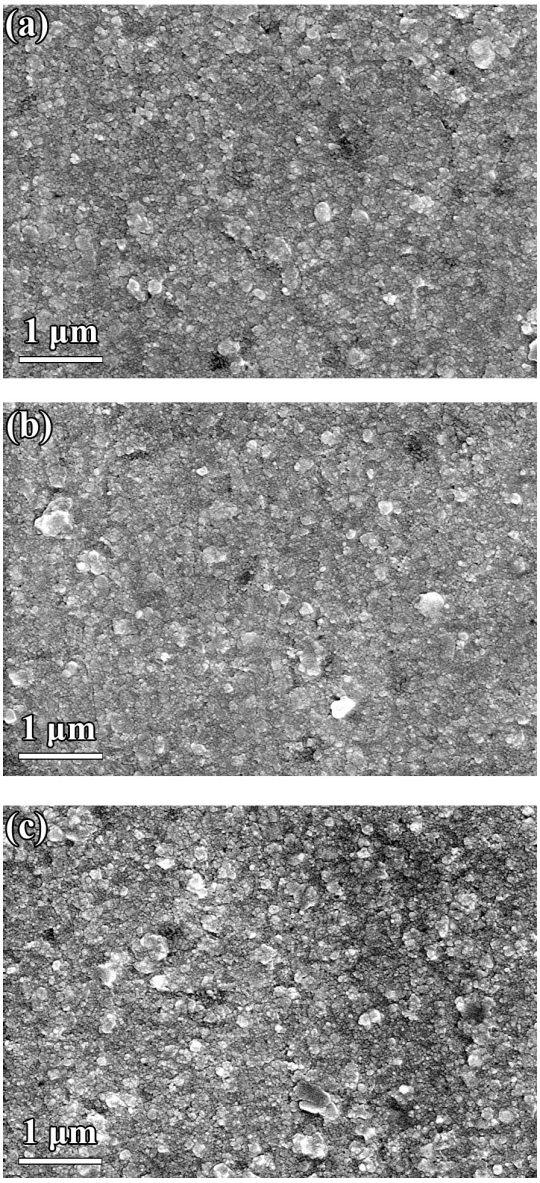

Fig. 1. SEM micrograph of the single-layer (a), double-layer (b), and triple-layer (c) film surfaces.

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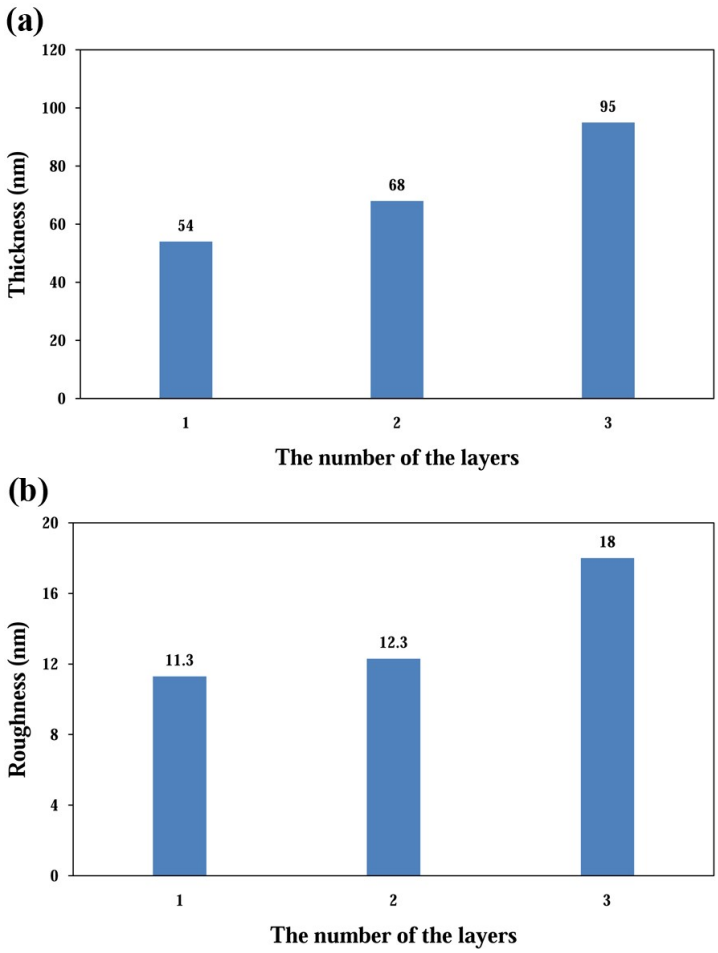

Fig. 2. Thickness (a) and roughness (b) values of the deposited films.

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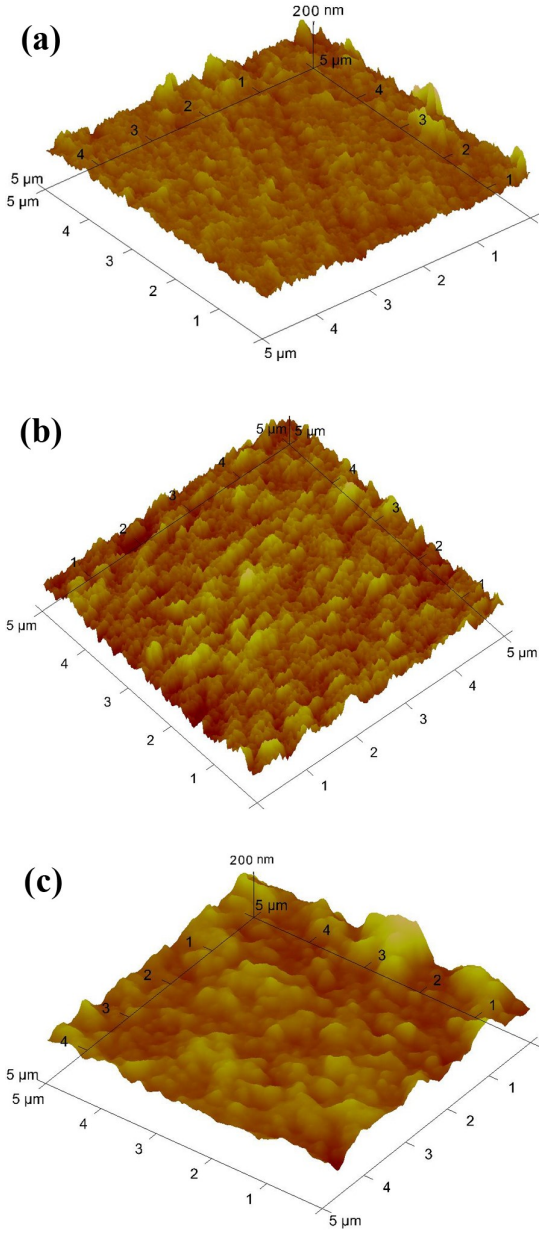

Fig. 3. Three-dimensional AFM image of the surface of the single-layer (a), double-layer (b), and triple-layer (c) thin films.

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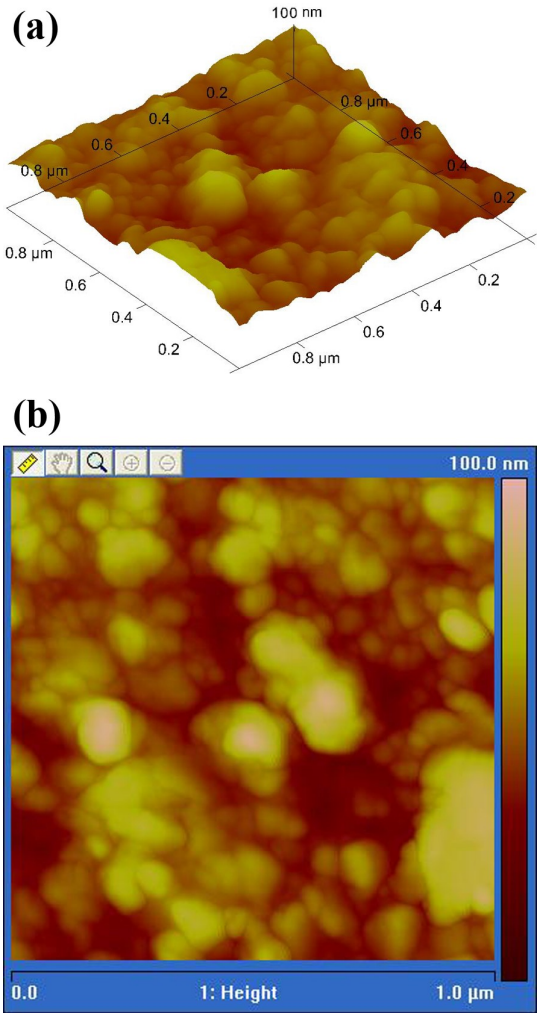

Fig. 4. Two-dimensional (a) and three-dimensional (b) AFM images of the monolayer thin film.

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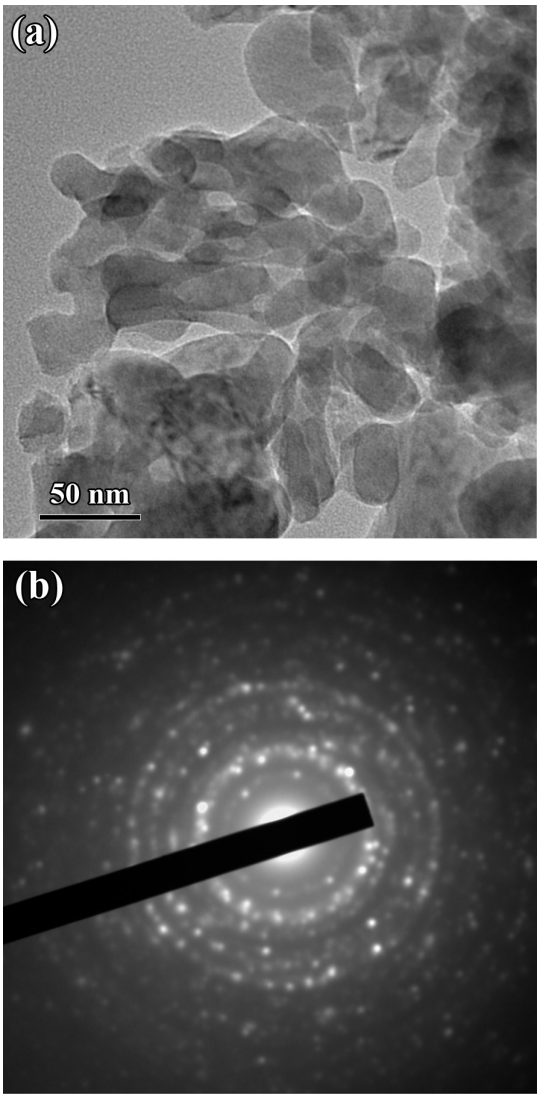

Fig. 5. TEM micrograph (a) and SAD pattern (b) of the calcined sample.