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Zirconium titanate thin film prepared by an aqueous particulate sol–gel spin coating process using carboxymethyl cellulose as dispersant

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Abstract

This paper deals with the preparation of $ZrTiO_4$ thin film by a novel aqueous particulate sol–gel deposition method using carboxymethyl cellulose as dispersant. The structural characterization was performed by X-ray diffraction, transmission electron microscopy, and scanning electron microscopy. According to the results, the amorphous xerogel crystallizes to polycrystalline $ZrTiO_4$ nanoparticles due to structural ordering conducted by calcination at 700 °C. A well-covering, crack-free, and homogeneous $ZrTiO_4$ thin film was processed,

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which is attributable to the efficient role of the dispersing agent in the aqueous sol. It was also found that the outermost layer of the coating surface consists of nanoparticles with 20 nm in size.

Keywords: Nanoparticles; Ceramics; Sol–gel preparation; Thin films

1. Introduction

Zirconium titanate ($ZrTiO_4$) thin films are considered especially in dielectric applications and more recently in biomedical applications [1,2]. Among various methods used to prepare thin films, the sol–gel process has notable advantages like high homogeneity, low sintering temperatures, and complex shape coating capability [3]. However, although widespread studies have been conducted on lead zirconate titanate, titania and zirconia films, little systematic work has been reported on $ZrTiO_4$ thin films deposited by sol–gel processes. Typically, dielectric properties of $ZrTiO_4$ films developed by a surface sol–gel process using butoxide precursors were studied [4]. Devi et al. [2] also investigated characteristics of $ZrTiO_4$ coatings processed by a non-hydrolytic sol–gel method employing titanium tetraisopropoxide and zirconium oxychloride precursors. But from both the scientific and technological viewpoints, facile, inexpensive and high-quality processing is markedly an essential concern. In this regard, recently a sol–gel method using chloride precursors was experimented to synthesize $ZrTiO_4$ nanoparticles [5]. Compared with polymeric sol–gel methods, the typical advantage of this facile route is employing chloride rather than alkoxide precursors to develop a product at lower cost. On the other hand, to deposit defect-free films by particulate sol–gel methods, a perfect dispersion of nanoparticles in the sol is obligatory.

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In this study, for the first time, carboxymethyl cellulose as a natural and inexpensive polymer was successfully employed as the dispersant to develop a $ZrTiO_4$ thin film by the particulate sol–gel method using chloride precursors.

2. Experimental

The sol–gel process detailed in Ref. [5] was used to synthesize nanoparticles, starting from 9.1 mmol of $ZrCl_4$ (Alfa Aesar, 99.5 %) and $TiCl_4$ (Alfa Aesar, 99.99 %). 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. The resultant sol viscosity was 80 mPa.S, measured using a Bohlin C-VOR rheometer. The sol was spin coated on stainless steel substrates at a speed of 3000 rpm. After drying at 80 °C for 1 h, firing was conducted 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. An amount of the sol was also dried at 80 ºC for 1 h and the obtained xerogel was calcined with the same heat treatment employed for the coating. The X-ray diffraction (XRD) spectra of the powders were recorded by a Bruker AXS Inco. diffractometer using Cu Kα radiation operating at 40 kV. Also, a transmission electron microscope (TEM, JEOL JEM-2100) operating at an acceleration voltage of 200 kV was used to evaluate the powder particles. The film surface and thickness were studied by a scanning electron microscope (SEM, Hitachi S-4800) and NanoSpec 3000 system (Nanometrics, CA, USA) respectively.

3. Results and discussion

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The XRD pattern of the xerogel and calcined powder is presented in Fig. 1(a). The broad halo pattern of the xerogel implies an amorphous structure; however, due to structural ordering the calcined powder shows a crystalline $ZrTiO_4$ pattern with a crystallite size of 20 nm, determined by the Scherrer equation. This behavior can be explained by considering the crystallization temperature of the material (690 °C) measured by differential scanning calorimetery [5]. Figs. 1(b) and 1(c) indicate the TEM micrograph and selected area diffraction (SAD) pattern of the powders. According to Fig. 1(b), the average powder particle size of the xerogel is approximately 5 nm. Also, the related SAD pattern indicates homogenous featureless diffraction halos attributed to an amorphous structure, as verified by XRD. In contrast, the calcined powder particles have an average size of 50 nm [Fig. 1(c)], signifying particle coarsening compared to the xerogel to reduce the surface energy. The high crystallinity of this powder results in distinct Debye-Scherrer diffraction spots in the corresponding SAD pattern. By comparing the crystallite size estimated by XRD and the particle size determined by TEM, it can be concluded that the calcined nanoparticles are polycrystalline in nature.

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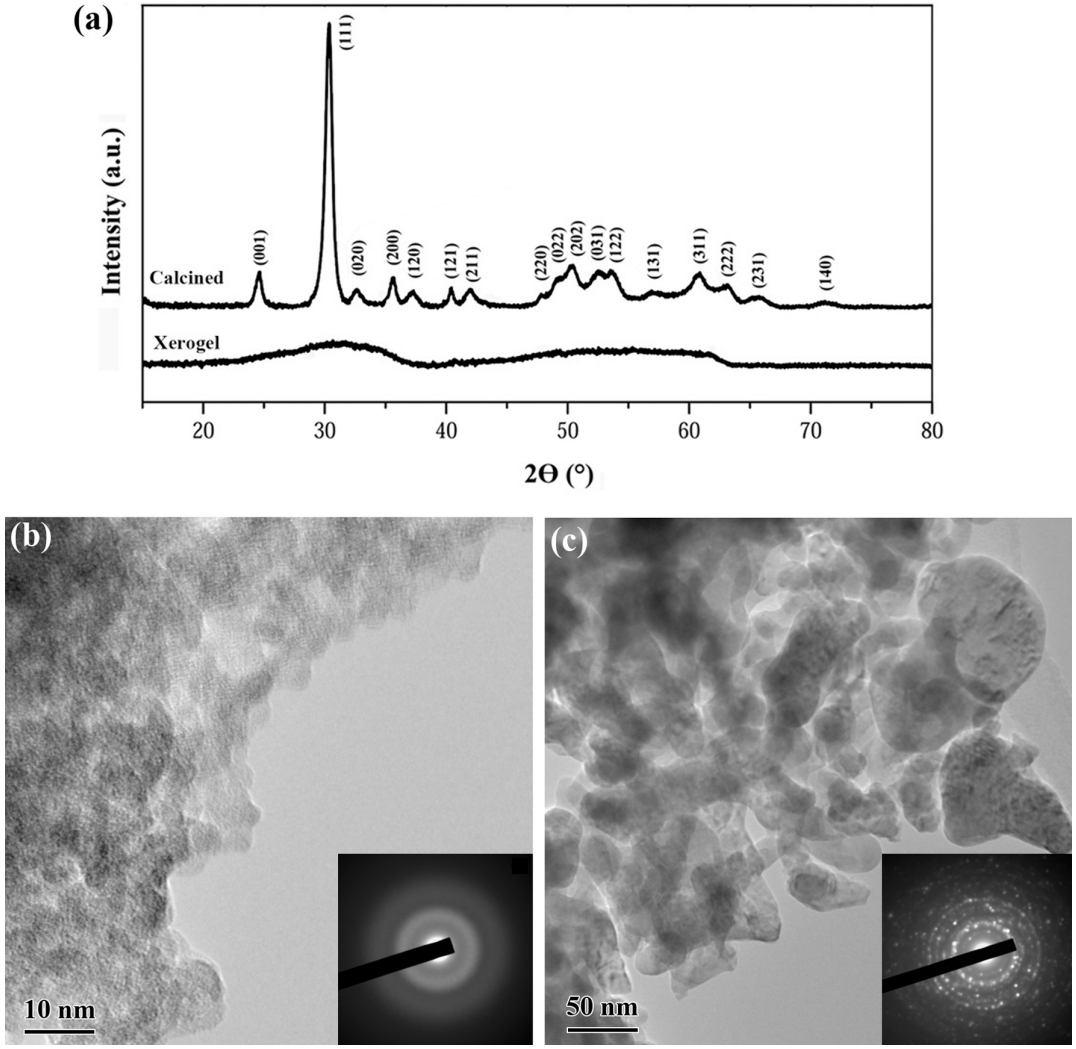

Fig. 1. XRD pattern of the xerogel and calcined powder (a), TEM micrograph and SAD pattern of the xerogel (b), and TEM micrograph and SAD pattern of the calcined powder (c).

With regard to the film preparation, to realize the role of CMC as the dispersant in the film quality, the SEM micrograph of the film in the absence of CMC is depicted in Fig. 2. It can be seen that in this circumstance, a desirable coverage is not obtained and separately coated zones (islands) with an average size of 50 μm are formed on the substrate [Fig. 2(a)]. Indeed, to decrease the surface energy, the amorphous nanoparticles have a strong tendency

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to agglomeration due to their hydrophobic nature and small size. Accordingly, the sol containing these nanoparticles does not cover the substrate uniformly, forms droplets rather than a liquid film, and leaves the islands. Moreover, pronounced cracks are observed on the islands, as shown in Fig. 2(b). Cracking is developed in the course of firing in the islands which locally provide significant thicknesses and undertake the removal of a high level of volatile materials and high shrinkage.

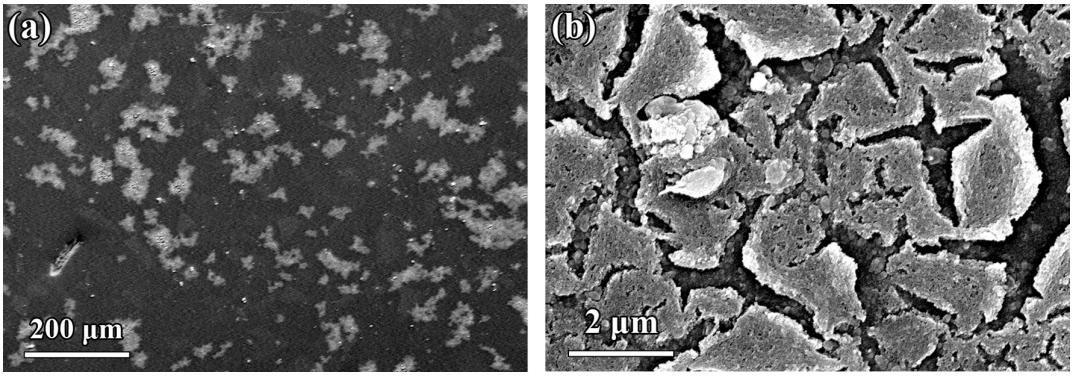

Fig. 2. SEM micrograph of the film deposited in the absence of CMC, in a low magnification (a) and in a higher magnification (b).

Fig. 3 demonstrates the SEM micrograph of the film with the CMC addition, in which the development of a relatively dense, smooth, well-covering, uniform, and crack-free coating is evident [Fig. 3(a)]. The film thickness was measured to be 54 nm, based on by the spectroscopic reflectometer. As can be seen in Fig. 3(b), the surface indicates particles/clusters of 30 nm to 250 nm in size with an average value of 80 nm. However, by decreasing the working voltage to 2 kV [Fig. 3(c)], it is clear that the outermost layer of the coating consists of nanoparticles with about 20 nm in size. In fact, the large particles

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observed in Fig. 3(b) can be sintered aggregates of smaller nanoparticles. The appearance of this surface feature can be explained as below. During sintering the nanoparticles grow, as focused in Fig. 1, and start appearing on the surface due to a mass transfer caused by transformation from a glass state to a crystalline one. 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) [6,7].

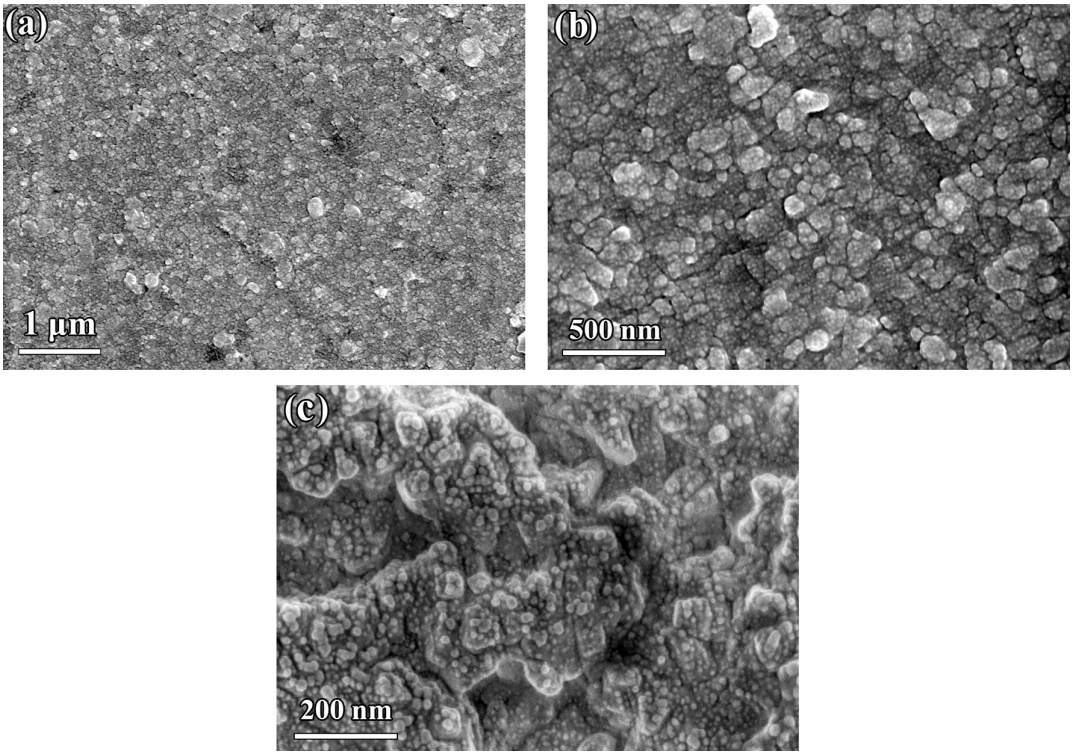

Fig. 3. SEM micrograph of the film which signifies the film quality at a low magnification (a) and SEM micrograph at higher magnifications obtained at a working voltage of 20 kV (b) and 2 kV (c).

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Since the firing process of the CMC-free and CMC-containing films was similar, the desirable characteristics of the CMC-containing film are attributed to the presence of CMC in the sol. Successfully, CMC as the dispersing agent makes the ceramic nanoparticles be negatively charged and depresses their hydrophobicity and agglomeration. Due to the interaction of the carboxylic group of CMC with the ceramic surfaces, CMC molecules adsorb on the interfaces of particle/aqueous solution, thereby forming a long chain polymer and anionic layer. In accordance with the steric stabilization theory [8-11], a strong steric repulsion between these particles is created, which leads to a high stability of the colloidal dispersion and uniform dispersion of the ceramic particles in the sol. Referring to the literature, the use of ammonium polyacrylate as a dispersant to avoid agglomeration of titania nanoparticles and thereby to obtain uniform films via a sol–gel dip coating process has been reported [12]. Every surfactant has an optimum effective level in a sol and excess concentrations have a negative effect. The optimum concentration is termed as its saturation adsorption limit. Overaddition can destabilize dispersion via depletion flocculation caused by an increase in osmotic pressure, thereby forcing particles together [13]. The effective amount of the surfactant used in this work is higher than that reported in Ref. [12]. It can be explained by the different natures of the particles and surfactant and also the smaller particles developed in this work having a higher surface area and thereby a higher saturation adsorption limit. On the other hand, the CMC-containing sol was a physically stable suspension without sedimentation after 2 weeks standing, in contrast to the CMC-free sol (Fig. 4). This is another evidence of the effective contribution of CMC to suppressing agglomeration of the nanoparticles. In the absence of the dispersant, the sol includes large and heavy agglomerates rather than separate nanoparticles and sedimentation is thereby in progress over time;

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however, in the presence of CMC, the strong steric repulsion between the particles suppresses agglomeration and provide a stable colloidal dispersion.

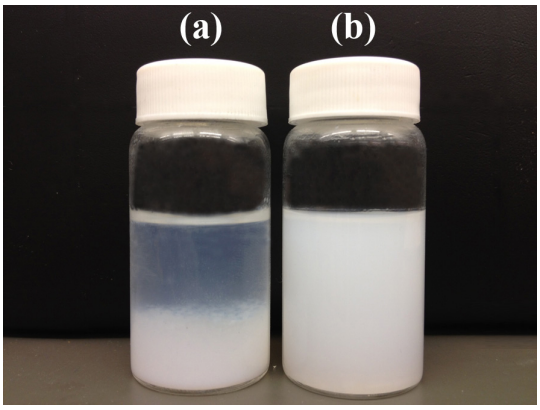

Fig. 4. Optical photo of the CMC-free (a) and CMC-containing (b) sols after 2 weeks standing.

As well as the significant contribution of CMC to the preparation of the desirable film, the film quality suggests the merit of the deposition and firing processes allowing the gradual removal of volatile materials (residual water and chloride). According to Ref. [5], the material presents a sharp weight loss when heating from 100 °C to 400 °C. Hence, the applied thermal cycle during firing allows the gradual removal of residual volatile materials and the preparation of the crack-free film. Moreover, the sol and thereby film include the nanoparticles of 5 nm in size which have significant particle boundaries. This high level of the boundaries assists the relief and dispersion of thermal stresses caused by thermal expansion mismatch between the film and substrate which is a powerful source for cracking.

4. Conclusions

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A sound $ZrTiO_4$ thin film was successfully prepared by a sol–gel method using CMC as the dispersant. Calcination of the amorphous xerogel at 700 °C led to crystallization and particle coarsening. The addition of CMC as the dispersing agent improved the suspension property of the sol and the film quality. Also, the outermost layer of the coating contained nanoparticles of nearly 20 nm in size.

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