International Journal of Natural Sciences Research
2017 Vol. 5, No. 3, pp. 50-54
ISSN(e): 2311-4746
ISSN(p): 2311-7435
DOI: 10.18488/journal.63.2017.53.50.54

STRUCTURE AND PROPERTIES OF $ZrTiO_4$ THIN FILMS PREPARED BY REACTIVE MAGNETRON CO-SPUTTERING WITHOUT HEATING

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Article History
Received: 2 August 2017
Revised: 7 September 2017
Accepted: 15 November 2017
Published: 19 December 2017

Keywords
Zrtio$_4$
Thin films
Optical properties
Dielectric constant
Co-sputtering.

ABSTRACT

$ZrTiO_4$ thin films were deposited by reactive dc magnetron co-sputtering method without heating. The crystal structure, surface morphology, thickness, optical and dielectric properties of the thin films were investigated. At sputtering currents above 2.0 A without heating $ZrTiO_4$ thin film was crystallization of the orthorhombic phase (111). The values of refractive index were ranged between 2.01 and 2.23 (at 650 nm). The optical packing density values were ranged between 0.85 and 0.96. From this study, it was observed that the refractive index values were strongly dependent on packing densities. The high dielectric constant width decreases from 74.3 to 43.3 when sputtering current increases, which is higher than other research.

Contribution/Originality: This study is one of very few studies which have a high degree of insulation of 43.3, which is higher than other research due to ZrTiO4 thin films were deposited by reactive dc magnetron co-sputtering system at Zr and Ti sputtering current of 2.5 A without heating

1. INTRODUCTION

Zirconium titanate ($ZrTiO_4$) is a small ceramic constituent material which is widely use of application to very good thermal and electrical properties and high resistance to heat and corrosive environment [1]. $ZrTiO_4$ thin films coatings have attracted much attention especially in dielectric applications which have high resistivity and dielectric constant (38-40) [2]. For size miniaturization, a low dielectric loss (tanδ ~10^{-2} to 10^{-3}) for high frequency selectivity and low signal attenuation and more [3]. Laterally, with the good dielectric properties, $ZrTiO_4$ thin films also exhibit good optical and electrical properties to find applications in antireflection coatings, wave guides for light, an insulator in electronic devices which requiring high permittivity and as protective coatings [2]. Due to their excellent optical, electrical and dielectric properties, it is important to study the dependence of film properties on the deposition conditions at the present time [4].

$ZrTiO_4$ thin films have been deposited by different techniques such as the dc magnetron sputtered $ZrTiO_4$ thin films have dielectric constants in the range of 35±7. The change in the dielectric constants due to the variation in the deposition temperature [5]. Moreover, those the correlation between the micro strain and dielectric loss of $ZrTiO_4$ thin films were studied. $ZrTiO_4$ thin films have been additional studied because of their excellent dielectric properties, such as the dielectric constant and dielectric loss of 38 and 0.006, respectively [6].

For engineering applications, the deposition of the $ZrTiO_4$ thin films should be simple processing and low cost. In the present study, $ZrTiO_4$ thin films were using dc magnetron sputtering which is a low cost preparation method. $ZrTiO_4$ thin films fabrication which has dielectric properties at low frequencies should be by using dc magnetron sputtering technique from the Zr and Ti targets have not been reported earlier. Moreover, Pamua, et al. [4] Growth of nanocrystalline zirconium titanate thin films at ambient temperatures using dc reactive magnetron sputtering from Zr and Ti metal targets placed in a single cathode. The present study demonstrates the dielectric constant of these films did not show much dependence on high frequency were not much to shows whereas the loss is higher at lower frequency region. The dielectric constant and loss of the films measured at frequencies in the range of

100 Hz-15 MHz were values between 37.0-46.5 and 0.007-0.03, respectively. In this paper, we designed the $ZrTiO_4$ thin film by a reactive dc magnetron co-sputtering. The methodical study of structural, microstructural, and dielectric properties of the films are reported.

2. EXPERIMENTAL PROCEDURE

2.1. Film Preparation

$ZrTiO_4$ thin films were deposited on Si (100) wafers, glass slides and stanless steels of the substrates by using a reactive dc magnetron co-sputtering system. Titanium (99.97%) and zirconium (99.95%) metals with a diameter of 3 inches were used as sputtering targets. Ultra high prerity Ar (99.999%) and O_2 (99.98%) gases were used as sputtering and reactive gas respectively. By reactive fixed flow rates of 4 sccm and 20 sccm, respectively. The target to substrate distance for both targets was 13 cm. A diffusion pump together with a rotary pump were used to achieve the base pressure of 5.0×10^{-5} mbar. Prior to deposition, the targets were pre-sputtered for 5 min in order to eliminate the contaminants from the target surfaces. The Zr sputtering current (I_{Zr}) and Ti sputtering current (I_{Ti}) were varied from 0.5 A to 2.5 A without heating. The deposition time for all prepared films was 40 min.

2.2. Characterization

The structural analysis of the $ZrTiO_4$ thin films were characterized by X-ray diffraction. The phases were compared with the Joint Committee on Powder Diffraction Standard (JCPDS) files. The crystallite size of the films were determined from Scherrer's formula. The surface and cross-sectional morphologies were examined by field emission scanning electron microscopy (FE-SEM: Hitachi, S4700). The transmittance spectra of the $ZrTiO_4$ thin films are analyzed by UV-VIS-NIR-spectrophotometer (Shimapzu, UV-3600) in the range of 200 nm to 2500 nm. Swanepoel's envelope method was used to determine the optical constant of the films [7]. The optical packing densities (p) of the films were calculated by using the relation is given by the bulk refractive index (n_b = 2.31) of $ZrTiO_4$ and n_f is the observed film refractive index and wavelength; λ = 650 nm [8]. The dielectric constant and dielectric loss (tanδ) were measured by using a precision impedance analyzer Agilent 4294A.

3. RESULTS AND DISCUSSIONS

3.1. Crystalline Structure

Fig-1 shows the XRD pattern of the $ZrTiO_4$ thin films at different sputtering currents of 0.5 A to 2.5 A without heating. This result showed that the thin films were crystalline, which exhibits an orthorhombic crystal structure (JCPDS 34-0415) and possesses α-PbO_2-type structure belonging to the *Pbcn* space group [9]. The $ZrTiO_4$ thin films were an amorphous structure at sputtering currents of 0.5 A, 1.0 A and 1.5 A respectively. And show preferred orientation in (111) direction at sputtering currents of 2.0 A and 2.5 A. The other observed XRD patterns are (011), (020), (200), (120), (201), (121), (022), (202), (122), and (311) peaks were shown also. Titania and zirconia thin films deposited by dc magnetron sputtering without substrate heating been reported to be amorphous earlier [10, 11].

The crystallite sizes are estimated from the full width at half maximum (FWHM) of the 111 peaks by using Scherrer's method (Table-1). The crystallite sizes are in the range of 14.95-20.06 nm at sputtering currents of 2.0 A and 2.5 A respectively. It is found that crystallite size increases with increasing sputtering currents.

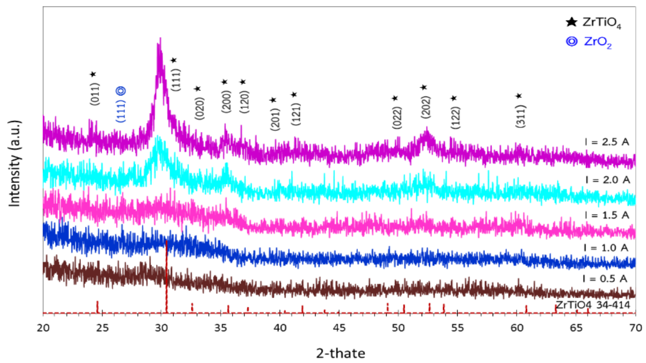

Fig-1. XRD patterns of the $ZrTiO_4$ thin films

Source: The result is a doctoral research. Analyzed with X-ray diffraction from School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi

Table-1. Crystallite size of the $ZrTiO_4$ thin films

I(A)	FWHM (β)	Crystallite size (Å)
0.5	-	-
1.0	-	-
1.5	-	-
2.0	0.550	14.95
2.5	0.410	20.06

Source: The result is a doctoral research by using Scherrer's method.

3.2. Cross-Sectional Morphology

Fig-2 shows the FE-SEM cross-sectional images of the $ZrTiO_4$ thin films. It is seen that the thickness of the films increases from 60 to 280 nm when sputtering current was increased from 0.5 A to 2.5 A without heating. These results are consistent with the XRD results, that are the intensity of XRD peaks increases with increasing sputtering current. It is clearly visible that the sputtering currents of 2.5 A present a columnar structure. These films are formed by a dense coalescence of columns propagating from the electrode to the film surface. It is concluded that increasing the sputtering currents of 2.5 A (Fig-2 (c)), promotes the formation of denser columnar structures, likely due to sputtering processes have much high energy and consistent with the results of the XRD patterns.

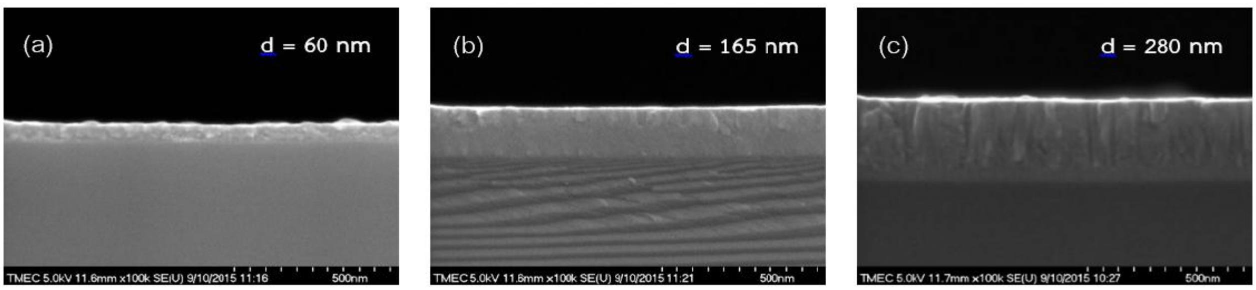

Fig-2. Cross-sectional FE-SEM morphology of the $ZrTiO_4$ thin films (a) 0.5 A, (b) 1.5 A, and (c) 2.5 A.

Source: The result is a doctoral research. Analyzed with field emission scanning electron microscopy from Thai Microelectronics Center:TMEC.

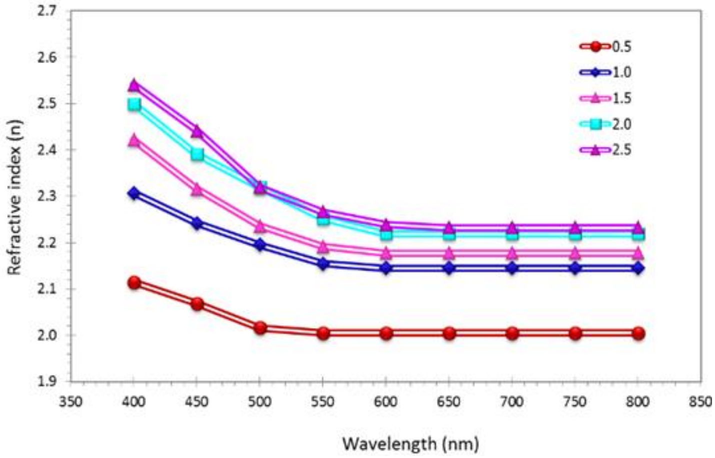

Fig-3. Refractive index of the ZrTiO4 thin films

Source: The result is a doctoral research. Analyzed with UV-VIS-NIR-spectrophotometer and calculate by Swanepoel's envelope method from Center of Excellence in Glass Technology and Materials Science (CEGM), NPRU

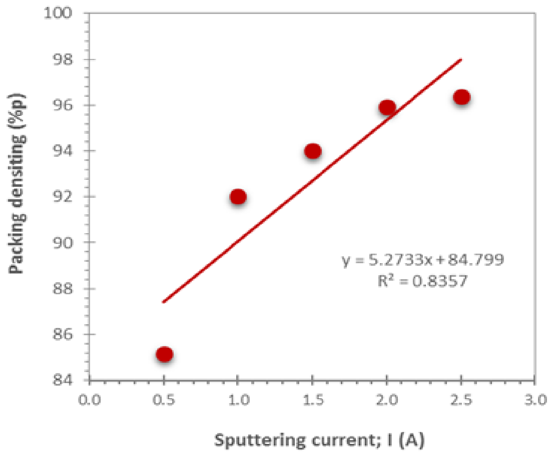

Fig-4. Packing density of ZrTiO4 thin films

Source: The result is a doctoral research. Calculated by using the relation is given by the bulk refractive index [8].

3.3. Properties of $ZrTiO_4$ Thin Films

The refractive index (*n*) of the films deposited on glass at different sputtering currents are shown in Fig-3. It is observed that refractive index increased with increase in sputtering currents. The values of *n* ranged between 2.01 and 2.23 (at 650 nm) [4]. It is seen that the film structure changes from a porous structure into a dense structure and have crystallite more than as the sputtering currents increases. These means that the packing density of the films increases together with crystallite addition are results in the increase in the refractive index. The optical packing density values were ranged between 0.85 and 0.96 (Fig-4). From this study it was observed that the refractive index values were strongly dependent on packing densities [4].

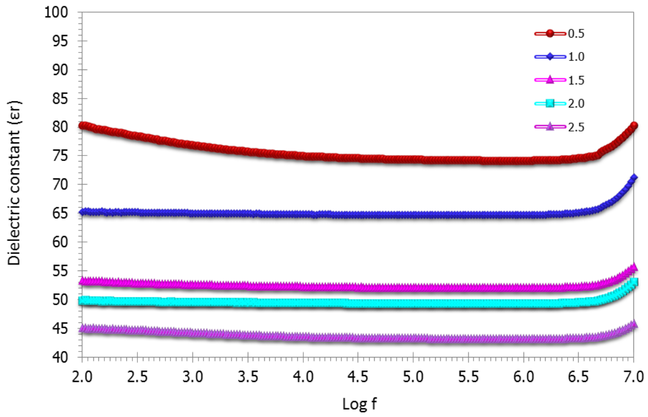

Fig-5. Dielectric constant of the ZrTiO4 thin films

Source: The result is a doctoral research. Analyzed with precision impedance analyzer from National Metal and Materials Technology Center (MTEC).

Fig-5 shows the dielectric properties of the $ZrTiO_4$ thin films at different sputtering currents of 0.5 A to 2.5 A. The dielectric constant and loss of the films were measured at frequencies in the range of 100 Hz-10 MHz and it is observed that as the sputtering current increases, the high dielectric constant width decreases from 74.3 to 43.3 for $ZrTiO_4$ thin films which were higher more than which other research because of higher energy [4, 12, 13].

4. CONCLUSIONS

$ZrTiO_4$ thin films were deposited by reactive dc magnetron co-sputtering method without heating. The XRD results showed that crystal structure of $ZrTiO_4$ thin films at sputtering currents above 2.0 A was crystallization of the orthorhombic phase (111). The values of refractive index ranged between 2.01 and 2.23 (at 650 nm). The optical packing density values were ranged between 0.85 and 0.96. From this study, it was observed that the refractive index values were strongly dependent on packing densities and crystalline of films. The high dielectric constant width decreases from 74.3 to 43.3 when sputtering current increases, which is higher than other research. In, conclusion the refractive index, packing density and dielectric constant depend on energy of sputtering currents.

Funding: This work was supported by the National Science and Technology Development Agency (NSTDA).
Competing Interests: The authors declare that they have no competing interests.
Contributors/Acknowledgement: All authors contributed equally to the conception and design of the study.

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