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Dielectric Properties of $ZrTiO_4$ Thin Films Prepared by Reactive DC Magnetron Co-sputtering

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Abstract: $ZrTiO_4$ is a small ceramic constituent material which has very good thermal and electrical properties. $ZrTiO_4$ thin films were deposited by reactive dc magnetron co-sputtering method. The crystal structure, surface morphology, thickness and dielectric properties were characterized by XRD (X-ray diffraction), AFM (atomic force microscopy), FE-SEM (field emission scanning electron microscope), and precision impedance analyzer respectively. These films were crystallization of the orthorhombic phase (111) of $ZrTiO_4$. The microstructure of well-crystallized $ZrTiO_4$ thin films had the surface morphology was smooth with 1.695 nmrms roughness. The high dielectric constant width decreases from 129.2 to 110.6 when sputtering current increases which are higher more than that had researched because of higher energy but impedance; |Z| increases from 1.97 to 2.47 kΩ. These results are consistent with the RMS roughness results, which are the RMS roughness decrease with increasing sputtering current.

Key words: $ZrTiO_4$, thin films, dielectric constant, magnetron sputtering.

1. Introduction

$ZrTiO_4$ (zirconium titanate) is a small ceramic constituent material which is widely used of application to very good thermal, 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 ($\tan\delta \sim 10^{-2}$ to 10^{-3}) for high frequency selectivity and low signal attenuation is more [3]. $ZrTiO_4$ thin films have been deposited by different techniques such as the DC magnetron sputtered $ZrTiO_4$ thin films have dielectric constants in the range 35±7. The change in the dielectric constants is due to the variation in the deposition temperature [4]. There are studied the correlation between the micro strain and dielectric loss of $ZrTiO_4$ thin films [5]. $ZrTiO_4$ 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. The dielectric properties of the ZT thin films at low frequencies by using DC magnetron sputtering technique from the Zr and Ti targets have not been reported earlier. Moreover,

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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 [7]. 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 from 100 Hz to 15 MHz were values between 37-46.5 and 0.007-0.03, respectively. The magnitude of leakage current density is 9.03×10^{-7} A/cm^2 at 10 MV/m for the films deposited at 40% OMP. 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 is reported.

2. Experimental Procedures

$ZrTiO_4$ thin films were deposited on Si (100) wafers, glass slides and stanless steels without external heating 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. Ar (99.99%) and O_2 (99.98%) gases were used as sputtering and reactive gas respectively. By reactive fixed flow rates of 4 and 20 sccm, respectively, the target to substrate distance for both targets was 13 cm. A diffusion pump together with a rotary pump was 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 at 0.5 A and 1.5 A. The deposition time for all prepared films was 40 min. Some of these films were heated at 600 °C compared with unheated.

The structural analysis of the $ZrTiO_4$ thin films was characterized by X-ray diffraction. The phases were compared with the JCPDS (Joint Committee on Powder Diffraction Standard) files. The crystallite size of the films was determined from Scherrer's formula. Raman measurements were taken with an RFS/100/S Bruker FT-Raman spectrometer equipped with a Nd:YAG laser in the 100-900 cm^{-1} spectral interval. The surface and cross-sectional morphologies were examined by atomic force microscopy (FE-SEM: Hitachi, S-4700) and field emission scanning electron microscopy (FE-SEM: Hitachi, S4700), respectively. The dielectric constant (ε_r) and dielectric loss (tanδ) were measured using a precision impedance analyzer Agilent 4294A. The dielectric constant of the films is calculated using Eq. (1)

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d} \quad (1)$$

where C is the capacitance in frequency, A is the area of overlap of the two plates measured in m^2, ε_r is the relative static permittivity of the material between the plates, ε_0 is the permittivity of free space and d is thickness of the pellet or film, measured in m.

3. Results and discussions

3.1 Crystalline Structure

Fig. 1a shows the XRD pattern of the $ZrTiO_4$ thin films deposited on Si (100) wafers at different sputtering currents of 0.5 and 1.5 A, which exhibits an orthorhombic crystal structure (JCPDS 34-0415) and possesses-PbO_2-type structure belonging to the *Pbcn* space group. The $ZrTiO_4$ thin films were amorphous structureat sputtering currents of 0.5 A and 1.5 A without heating [8] and show preferred orientation in (111) direction at sputtering currents of 1.5 A with heat 600 °C. The other observed XRD patterns are (011), (020), (200), (120), (201), (121), (211), (220), (022), (202), (122), (311), (222) and (320) peaks. The crystallite size increases were 53.124 nm at sputtering currents of 1.5 A with heat 600 °C.

Raman spectroscopy of $ZrTiO_4$ was shown orthorhombic symmetry (space group Pbcn) [9] and two formula units in a unit cell which confirm by Fig. 1b. Only $ZrTiO_4$ bands were observed in 100-900 cm^{-1}

region of the Raman spectra of sintered ceramics. In the Raman spectrum at sputtering currents of 1.5 A, expected $ZrTiO_4$ bands were resolved: 136, 164, 258, 342, 393, 484, 560, 640, 763 and 792 cm^{-1} [1].

Fig. 2 shows the AFM surface images of the $ZrTiO_4$ thin films deposited on Si (100) wafers at different sputtering currents. The average root-mean-square (RMS) roughness of $ZrTiO_4$ thin films was shown in Table 1. It is observed that the RMS roughness decreases from 3.602 to 0.976 nm as the sputtering current were increased from 0.5 to 1.5 A without heating. But the RMS roughness increases from 1.511 to 1.695 nm when heat 600 °C.

3.2 Cross-Sectional Morphology

Fig. 3 shows the FE-SEM cross-sectional images of the $ZrTiO_4$ thin films. It may be noted from Fig. 3a that the film exhibited uniform cross-sectional thickness and the film thickness was about 60 nm at sputtering currents of 0.5 A. It is observed that as the sputtering current increases, the columnar of increases and results in the increase of the lateral grain size. The grain size of the $ZrTiO_4$ thin films increased with increasing crystalline temperature [6]. 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 1.5 A (Fig. 3d), 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.

The film thickness can be determined from the images in Fig. 3 and the results are shown in Table 1. It is seen that the thickness of the films increases from 60 to 165 nm when sputtering current is increased from 0.5 to 1.5 A without heating. These results are consistent with the XRD results, which are the intensity of XRD peaks increases with increasing sputtering current.

3.3 Dielectric Properties

Table 2 shows the dielectric properties of the $ZrTiO_4$ thin films at different sputtering currents of 0.5 and 1.5 A. And 1 MHz dielectric properties of $ZrTiO_4$ thin films at sputtering currents, it is observed that as the sputtering current increases, the high dielectric constant width decreases from 74.3 to 52.1 for $ZrTiO_4$ thin films without heating [8] which are higher more than which had researched because of higher energy. Moreover $ZrTiO_4$ thin films with heat 600 °C are valuable high dielectric constant has increased to 129.2 [7]. But impedance;|Z| increases from

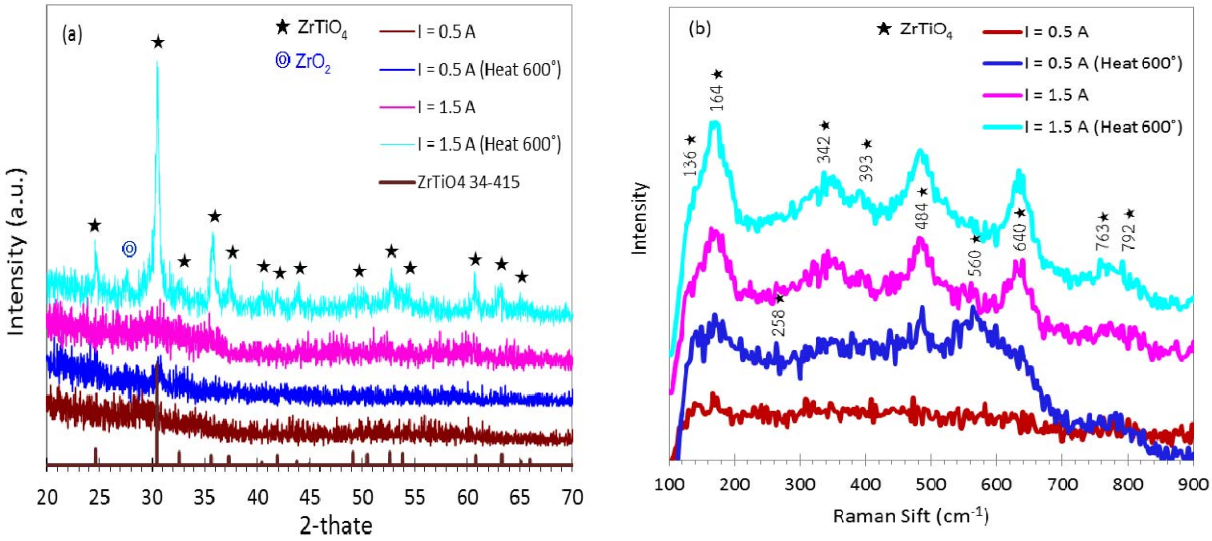

Fig. 1 $ZrTiO_4$ thin films deposited at various sputtering currents (a) XRD patterns and (b) Raman spectroscopy.

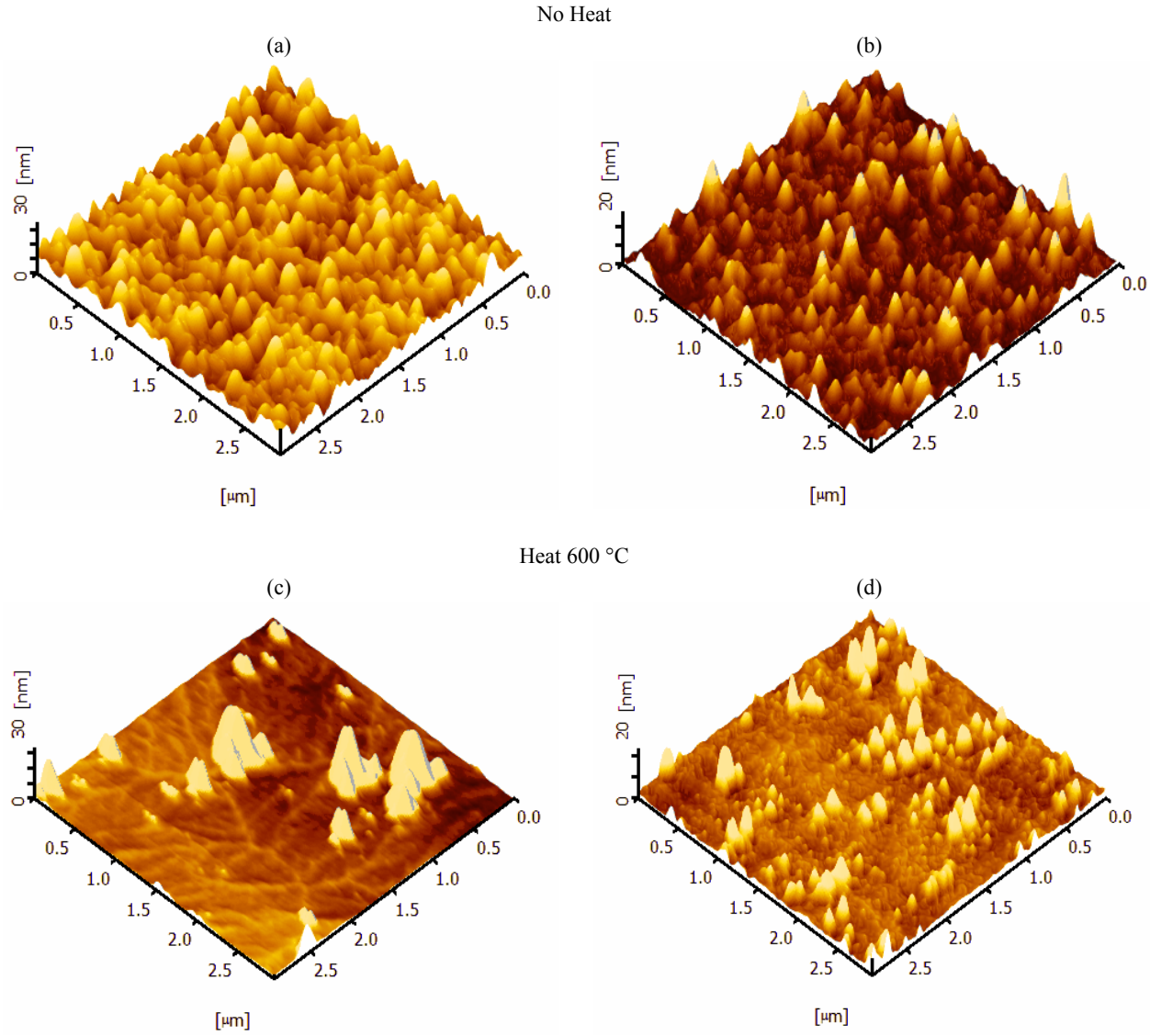

Fig. 2 AFM images of the $ZrTiO_4$ thin films at no heat [(a) 0.5 A, (b) 1.5 A] and at heat 600 °C [(c) 0.5 A, (d) 1.5 A].

Table 1 Crystallite size, thickness and roughness of the $ZrTiO_4$ thin films.

	Vary I	FWHM (β)	Crystallite size (Å)	Thickness (nm)	Roughness (nm)
No heat	0.5	-	-	60	3.602
	1.5	-	-	165	0.976
Heat 600 °C	0.5	-	-	60	1.511
	1.5	0.155	53.124	190	1.695

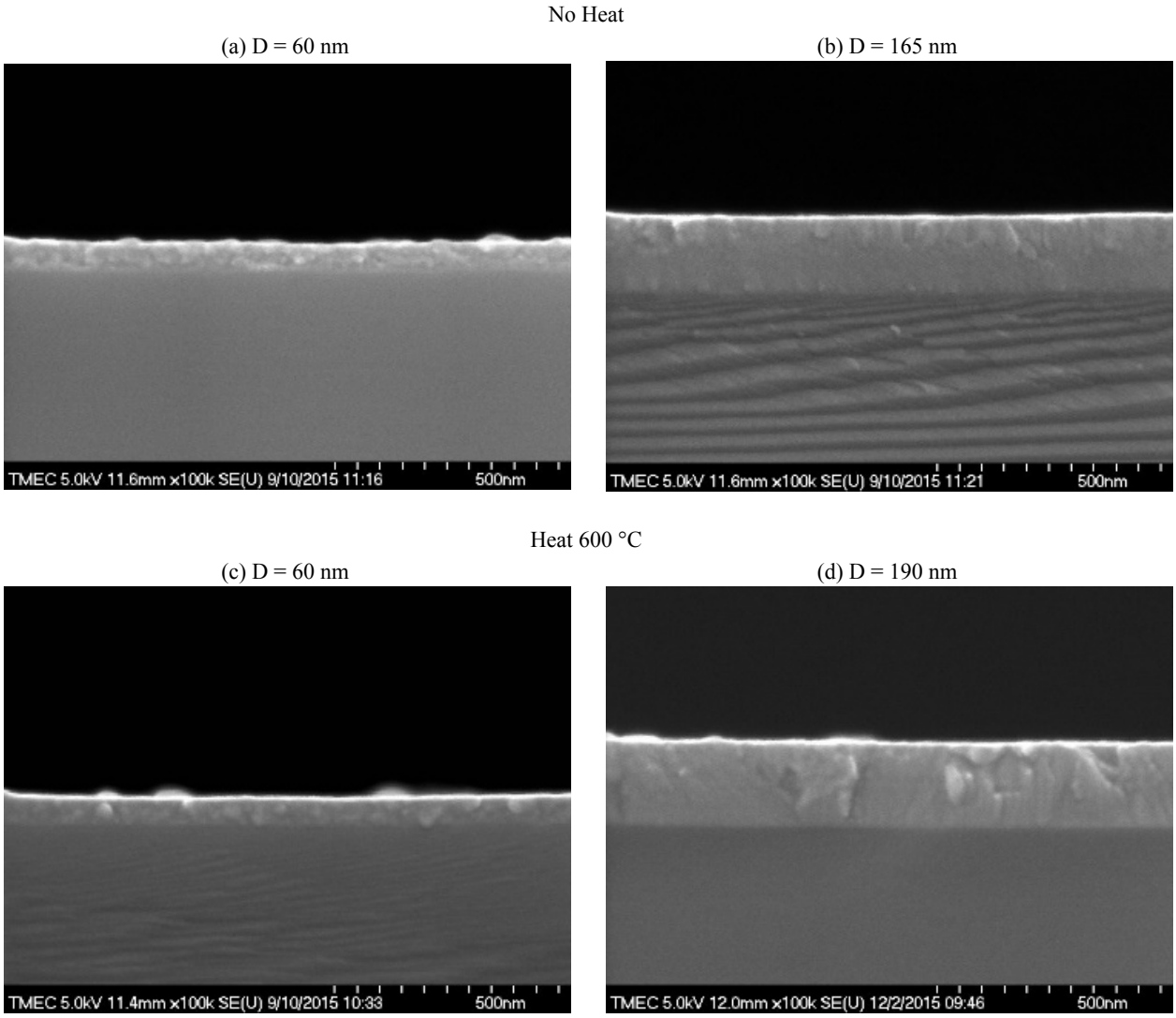

Fig. 3 Cross-sectional FE-SEM morphology of the $ZrTiO_4$ thin films at no heat [(a) 0.5 A, (b) 1.5 A] and at heat 600 °C [(c) 0.5 A, (d) 1.5 A].

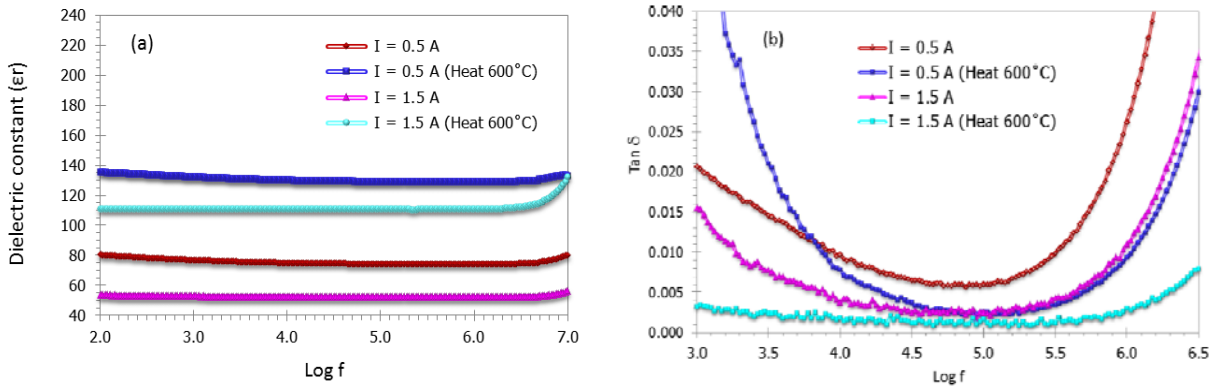

Fig. 4 $ZrTiO_4$ thin films deposited at various sputtering currents (a) dielectric constant (f = 100 kHz); (b) dielectric properties (f = 100 kHz).

Table 2 Dielectric properties at *f* = 100 kHz of the $ZrTiO_4$ thin films.

	Vary I	Dielectric propoty		
		εr	tan δ	|Z| (kΩ)
No heat	0.5	74.3	0.006	2.01
	1.5	52.1	0.002	3.89
Heat 600 °C	0.5	129.2	0.007	1.97
	1.5	110.6	0.002	2.47

2.01 to 3.89 kΩ for $ZrTiO_4$ thin films without heating and ;|Z| increases from 1.97 to 2.47 kΩ for $ZrTiO_4$ thin films with heat 600 °C the results are shown in Table 2.

4. Conclusions

$ZrTiO_4$ thin films were deposited by reactive dc magnetron co-sputtering method. The results showed that, from XRD results crystal structure of $ZrTiO_4$ thin films corresponding in the orthorhombic (111). The microstructure of well-crystallized $ZrTiO_4$ thin films was the surface morphology was smooth with 1.695 nm RMS roughness. The high dielectric constant width decreases from 129.2 to 110.6 for $ZrTiO_4$ thin films without heating when sputtering current increases but impedance; |Z| increases from 1.97 to 2.47 kΩ. This result is consistent with the RMS roughness result, that is the RMS roughness decrease from increasing sputtering current.

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