August 21, 2019

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To cite this article before publication: Nurhamizah Ahmad Rusli *et al* 2019 *Mater. Res. Express* in press <u>https://doi.org/10.1088/2053-1591/ab3907</u>

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## Bias voltage dependent structure and morphology evolution of magnetron sputtered YSZ thin film: A basic insight

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#### Abstract

YSZ thin films (YSZTFs) with controlled structure and morphology are desirable for low temperature solid oxide fuel cells (SOFCs). We report for the first time the bias voltage (40 V and 120 V) dependent structural and morphological evolution of YSZ thin films grown via radio frequency magnetron sputtering (RFMS) technique. The optimum sample was annealed at 600 °C to achieve an improved ionic conductivity. As-prepared YSZTFs were characterized using various analytical tools. Glancing angle X-ray diffraction (GAXRD) pattern of YSZTFs revealed the existence of non-columnar structure (cubic phases) with preferred growth along [200] lattice orientation. YSZTFs grown at 120 V displayed good homogeneity and uniformity (100 nm thick and crystallite size in the range of 10–12 nm) accompanied by large microstrain along [111] lattice orientation. The bias voltage dependent alterations in the morphology of YSZTFs (grain compactness, size, shape, distribution and surface roughness) were clearly manifested in the FESEM and AFM images. Raman and FTIR spectra of YSZTFs disclosed the formation of tetragonal and cubic phases. An in-depth data analyses suggested the successful incorporation of Yttria into the zirconia lattice. Annealed film exhibited improved polycrystallinity and evolved morphology. These achieved YSZTFs could be effective electrolyte for low temperature SOFC operation.

Keywords: Yttria Stabilize Zirconia Thin Film, RF Magnetron Sputtering, Bias voltage,

SOFC, Structure, Morphology

### 1. Introduction

In recent times, ceramic coating or film as solid electrolyte such as yttria-stabilized zirconia (YSZ) became advantageous for efficient SOFC operation. However, most of the popular electrolytes referring to solids that possess high conductivity are either anions or cations, not usually both [1–3]. The roles of solid electrolyte with anion conduction ( $O^{-2}$ ) that facilitates ionic movement from one site to another at the operating temperature range of 300–500 °C have already been demonstrated [4–7]. Over the years, to improve the electrolytic performance of YSZ material several strategies have been adopted including the manipulation of ionic defects, concentration, mobility, structural orientation, microstructure, grain boundaries and interfaces of hetero-structures [8–11]. Despite many dedicated efforts outperforming YSZ electrolyte is far from being achieved.

Numerous studies revealed that YSZ nanostructures grown via radio frequency magnetron sputtering (RFMS) technique are appreciably distinct than those produced by other methods [12–15]. Wang et al. [16] used RF reactive sputtering and co-sintering approach in the temperature range of 1150 to 1350 °C to produce cubic YSZ crystallites with small grain size and thickness of 10  $\mu$ m. Later, Solovyev et al. [17] acknowledged YSZTFs sintered at 1250 °C could significantly affect the non-columnar structure and lowered the thickness (3  $\mu$ m). Federico et al. [8] showed that YSZTFs of small thickness (100 nm) could possess void of blocking grain boundaries perpendicular to the current flow, thereby reduces the contribution of electron conductivity This was consistent with the properties of YSZ ceramic containing 8 mol% of Y<sub>2</sub>O<sub>3</sub> with high dielectric tenability and relatively low dielectric loss [18].

Yet, not many studies have been performed to examine the structural and morphological evolution of YSZTFs deposited via RFMS technique with varying growth parameters (bias voltage, RF power, annealing temperature, substrate types, and so forth), mainly due to costly equipment installation [19]. It has been realized that substrate bias voltage can be used to

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generate response of polymorph solid oxide with varieties of crystal structures including tetragonal, monoclinic and cubic [20]. The limitation of RFMS technique can be overcome by some innovations where low RF power can be utilized without varying the substrate temperature. According to Tolstova et al. [21], bias substrate assistance could be effective for the epitaxial growth of platinum (Pt) and gold (Au) onto MgO substrate (dielectric). The bias substrate assisted technique could successfully enhance the surface adatoms mobility, the number and density of nucleation sites, film density and columnar grain growth [22].

Most of ceramic materials that have been intended so far for SOFC applications possessed very low thermal conductivity and weak intrinsic shock resistance, indicating their possible catastrophic failure when subjected to excessive heating [23,24]. Moreover, DC magnetron sputtering is ineffective for insulating target because of no current flow through it. This shortcoming was surmounted using an alternating current (AC) at high frequency (13.56 MHz), where the sputtered ions and electrons at such frequency have very dissimilar mobilities in the fluctuating field [25]. It was shown that the application of DC voltage to the substrate (negative potential) could cause a potential drop within the substrate sheath due to the nonlinear behaviour of plasma potential, which could alter the discharge characteristics significantly [26]. This condition could change atomic arrangements in the substrate structure, resulting in an enhanced diffusivity for atoms bombardment. Currently, the high melting temperature (2730 °C) has been identified as the most influential factor for the cubic YSZTFs growth. So far, the effects of substrate bias voltage on the structure and morphology of YSZTFs and dielectic material grown using RFMS technique have not been well explored [27][28].

Present work evaluated the effect of substrate bias voltage (40 V and 120 V) on the microstructures, crystalline phases and morphologies of YSZTFs (thickness under 300 nm)

deposited using RFMS. Furthermore, the optimum film grown at 120 V was annealed at 600 °C to improve the oxide ion conductivity useful for SOFC implementation.

### 2. Experimental

High purity (99.99%) YSZ target containing 8 mol% of  $Y_2O_3$  was used to deposit the YSZTFs on glass substrate (SiO<sub>2</sub>) having dimension of 20 mm × 10 mm × 2 mm. RFMS system (Kurt J. Lesker model PSP5004) equipped with a turbo-molecular pump (base vacuum pressure of  $6.66 \times 10^{-6}$  mbar and power of 100 W) was used to deposit such films. Proposed TFs were prepared at room temperature in the presence of argon gas flow attached to a rotational platform that revolved with the speed of 3 rpm. The sputtering pressure, argon flow rate and deposition time were fixed at 6.66 mbar, 100 sccm and 1 hour, respectively. The influence substrate bias voltages (0, 40 and 120 V) on the structure and morphology of YSZTFs (without and with annealing) were determined. Hereafter, samples deposited at 0, 40, 120 V (without annealing) and the one deposited at 120 V under 600 °C annealing for 1 hour are labelled as SOV, S120V and S120V-600C, respectively.

Crystalline phases of synthesized YSZTFs were identified by glancing angle X-ray diffraction (GAXRD, Roguku diffractometer) technique equipped with a diffracted-beam graphite monochromator. It used CuK<sub> $\alpha$ 1</sub> radiation (wavelength of 1.5406 Å), glancing angle of 1.5°, scanning angle (2 $\theta$ ) in the range of 20 to 90°, scanning rate of 5°/min and a step size of 0.05°. The surface morphologies of YSZTFs were imaged using field emission scanning electron microscopy (FESEM, Carl Zeiss-Crossbeam 340 model) operated at 2 kV. All films were pre-sputtered using Pt to reduce the charging effect originated from their nonconductive nature. Raman spectra of YSZTFs in the range of 800–100 cm<sup>-1</sup> were recorded using a HORIBA LabRAM HR Evolution Model Raman Spectrometer. It was equipped with a green solid state diode laser system of wavelength 633 nm (excitation source) and 2048 element

linear silicon CCD array (detector). Structural properties of YSZTFs in the range of 4000–400 cm<sup>-1</sup> was analyzed using Fourier Transform Infrared (FTIR) Spectrophotometer (Perkin-Elmer Model 1725×). Elemental analyses were performed using Energy Dispersive X-Ray (EDX). Meanwhile, surface topography and size distribution was imaged using a NanoNavi AFM interfaced with SPIWin software.

#### 3. **Results and Discussion**

#### **3.1 FESEM Images**

Figure 1 shows the FESEM images (top and cross-sectional view) of all as-deposited YSZTFs. Film deposited without bias voltage (0 V) consisted of uniform surface with merging tendency of some granular clusters, which was attributed to the coalescence of tightly bound inter-granular growth (Figure 1(a)). Such grains were more strongly bound together than coupled to the substrate because of low adatom diffusivity. Besides, the lower mobility of the depositing particles was responsible for enhanced shadowing effect of the sputtered species emerged from multidirectional plasma flow [29]. According to Jung et al. [30], this type of nucleation of the sputtered species was indeed accountable for the columnar growth. Such growth was ascribed to the spatially separated impingement of grains (nuclei) onto the grain boundaries because of the low substrate or annealing temperature assisted processes that could result in rapid solidification without grain growth. The morphology of YSZTF deposited at 40 V (Figure 1 (b)) revealed inter-connected grains with some surface discontinuity, which could be due to the migration of adatoms from smaller to bigger cluster. The bigger clusters could act as the strong replicating or binding media to other atoms coupling. Furthermore, few columnar shaped grains were also observed in the cross-sectional image. In fact, the grain growth became noticeable at 40 V. Film deposited at 120 V showed the presence of dense and uniform distribution of small particles (Figure 1 (c)), which was

ascribed to the rapid enhancement of adatom mobility and subsequent modification of the nucleation process. High energetic electrons at this bias voltage could improve the particles bombardment, thereby layer by layer growth was observed. The rearrangements of crystallites with reduced size and thickness was attributed to the development of intrinsic stress within the YSZTFs [28][31]. Further annealing of the film at 600 °C was found to enhance the homogeneity (Figure 1 (d)), indicating high mass diffusion inside the YSZ films and achievement of denser columnar structures. Figure 1 (A-D) shows FESEM images (cross sectional) of YSZTFs. The S120V thin film revealed lowest thickness despite a uniform layer and interlocking with the substrate, thus contributed to dense structures. This could be due to the increased amount of YSZ formation at higher bias voltage. This uniformity is believed to be caused by adatom mobility increase hence produce adverse effect for the YSZ thin film nucleation. The estimation energetic electron produced at 120 V over the area roughly improve the particle bombardment. While layer by layer growth is observed. These structures were dense, but their arrangement of crystallite size was decrease so that, reduced thickness existed due to many intrinsic stress of the YSZ thin film. FESEM cross-sectional analysis indicated that the deposited S120V film was sufficiently stable to maintain the growth, resulting in good interlayer between substrate and thin film. Furthermore, the observed increase in the thickness of S120V-600C was ascribed to the influence of combined annealing that allowed the the YSZ layer to replicate the texture, leading to thicker and denser film. This annealing stage technique indicated that high mass diffusion inside the YSZ films seems to promote denser (columnar structures merge). Meanwhile, the resulting thin film of SOV and S40V did not merge together completely, resulting a gap between the substrate interfaces and the YSZTFs.

It is worth noting, the bias voltage driven nucleation and growth of amorphous as well as ceramic materials is a complex process that needs further clarification. A simple relation Page 7 of 36

exists between the supplied voltage to the substrate and the substrate surface bombardment by positive ions alongside the target cathode. The overall evolution of the surface morphology due to bias voltage and annealing can be explained as follows. First, plasma is generated by electrical field applied to low pressure in range 1mTorr-10 Torr. At low pressure, high voltage electric can cause vacuum breakdown and produce plasma which consists ions, electrons and reactive species. The electrical energy supplied to the sputtering system allowed the ejection of atoms and secondary electron, wherein the generated heat was absorbed by the target and the substrate. Next, free electrons play a role to maintain the plasma, while ions and radicals contribute to film growth. Furthermore, with the application of bias voltage a gradual densification of the film could occur due to ion impacts so called ion-peening process. According to Seo et al. [26], the electron energy distribution function (EEDF) could make similar contribution to the electron density due to the variation of substrate bias voltage. At higher bias voltage such as 120 V, the columnar grain structure could be disrupted and the microstructures transformed to equiaxed. In other words, the grains were strongly overlapped during the growth, allowing the stacking of multiple crystallites onto each other. It was affirmed that the stretching of single grain on the entire film surface and the formation of noncolumnar microstructure devoid of pinholes are beneficial for electrolytic applications.

Film deposited at 120 V revealed the lowest thickness of 115.4 nm than others. The thickness of the film deposited at 120 V was further increased from 115.4 nm to 208.4 nm upon annealing at 600 °C. Large decrease in the film thickness from 225.2 nm (S40V sample) to 115.4 nm (S120V sample) indicated significant alterations in the grain size and distribution because of bias voltage. Sillassen et al. [28] also acknowledged some significant effect of oxide ion transport along dense grain boundaries of YSZTFs due to small and homogeneous grains. Nedelec et al. [32] claimed that bias-assisted sputtering could transform the columnar structure into a non-columnar one. Application of bias voltage could influence the dense

microstructure and morphology of YSZTFs by accelerating the positive argon atoms towards the substrate. It was suggested that one must constantly monitor the bias voltage to avoid the substrate surface sputtering by high energetic argon atoms, which in turn could crack the substrate.

#### **3.2 GAXRD Pattern**

Figure 2 illustrates the GAXRD patterns of the studied YSZTFs. It revealed seven crystalline peaks positioned at 30.58, 35.28, 50.67, 59.85, 62.01, 73.00 and 83.37° assigned to different lattice orientations that matched with ICSD code 98-018-1237 for YSZ cubic phases. The existence of intense peaks along [111], [200], [220] and [311] lattice directions together with relatively weaker peaks along [222], [004] and [024] lattice planes confirmed the polymorph orientations of the YSZTFs as reported by others [8][16]. Film deposited at 0 V displayed amorphous nature, but other samples exhibited high polycrystallinity with preferred lattice orientation along [111]. The intensities of all cubic peaks were appreciably improved due to annealing at 600 °C (S120V-600C sample). Furthermore, the observed weakening in the intensity of all peaks for S120V sample than that of S40V except [111] orientation clearly indicated the appearance of lower polycrystallinity of the film at higher bias voltage (120 V). Nonetheless, the annealing at high temperature could enhance the polycrystallinity (nucleation, growth, morphology and orientation of crystallites along preferred lattice planes) of S120V-600C sample. Scherrer's formula was used to calculate the mean crystallite size wherein the full width at half maximum (FHWM) for the significant XRD peaks were chosen. The estimated mean crystallite size for S120V-600C sample was 17.39 nm. This disclosure was attributed to the annealing temperature assisted strain relaxation mechanism via annihilation of ionic defects such as oxygen vacancies.

Figure 3 displays the refinements of the GAXRD pattern for first four intense cubic peaks corresponding to [111], [200], [220] and [311] lattice orientations. The S120V-600C sample revealed the highest peak intensity for the most preferred lattice orientation along [111], indicating best polycrystallinity. Meanwhile, the observed shift in  $2\theta$  for all peaks was attributed to the involvement of lattice microstrain in the films. The appearance of higher peak intensity along [200] lattice orientation for S40V sample compared to other YSZTFs was ascribed to the formation of less dense but wider columnar structure for the former one as supported by FESEM results. Yet again, this finding was consistent with the observation of Hong et al. [33]. It was shown that the lower intensity along [200] lattice orientation could lead to the formation of dense, less defective, and restrained columnar grain. Sonderby et al. [27] prepared YSZTFs on Si (001) substrate using reactive pulsed DC magnetron sputtering technique. The XRD analyses of the grown YSZTFs revealed cubic phases with varied correlated columnar microstructures of mean diameter 200 nm. The [200] peak intensity corresponding to these restrained columnar structure was more intense than the growth along [111] orientation, wherein the positions of [200] and [311] were found to be at lower angles than ours. Such shift in the  $2\theta$  values at lower angles could be due to the formation of smaller grains and microstrain mediated uniform dispersion of these nanocrystallites over the entire substrate surface.

Figure 4 depicts the microstarin in the studied YSZTFs grown along preferred lattice planer orientations. Williamson and Hall equation was used to estimate the mean crystallite size and microstrain involved along different lattice orientations. The nanocrystallite size in each YSZTF was calculated by considering the most intense peak. Irrespective of the bias voltage and annealing temperature, nanocrystallites grown along [220] lattice orientation revealed the highest microstrain. Overall, both nanocrystallite sizes and microstrains in the studied YSZTFs displayed wide variations, indicating the impact of bias voltages on the YSZ

microstructures. Based on the estimated microstrain values it was asserted that S120V-600C sample was the optimum one (0.00296). Occurrence of such lowest microstrain along [200] direction than other orientations was attributed to the presence of weakest atomic packing density because of high surface energy and good interfacial interactions. While, the highest calculated microstrain value (0.00427) for S40V. Upon annealing, the lattice strain of S120V-600C sample was slightly reduced compared to other films which indicated lower lattice distortion, an effect of higher substrate bias voltage (120 V) and heating. At higher substrate bias, loosely bonded atoms were ejected from the substrate surface by the bombarding ions from the target, thereby increased the barrier energy of migrating oxygen vacancy. In short, the bias voltage induced microstrain played significant role in the formation of good quality nanoscale heterostrusture or layered YSZTFs advantageous for SOFC applications.

Kushima and Yildi et al. [35] claimed that for brittle ceramic film like YSZ an optimal strain level exists in a coherent hetero-interfaces at the nanoscale. Thus, the effect of microstrain in YSZTFs that arise due to interfacial mechanism of heterostructures could alter the electron energy levels symmetry to provide improved charge transfer and mobility. Some studies on the ionic properties of enabled stipulation of heterogeneous structure revealed that heterophases could possess faster ionic conduction pathways compared to bulk and homophases [36]. In this study, based on the observation regarding the thin film growth, the nucleation process of a YSZ thin film is usually very complex. However, the nucleation process can be hypothesized into heterogeneous nucleation because this nucleation is contributed from deposition medium. For example in sputtering vacuum system, the kinetic energy of atoms and ions is transfer over the thin film area and become heated. The estimation temperature produced over the area roughly 200 C° starting after the deposition. The produced temperature in the system leads to the non-crystallite thin film because the low driving force. Therefore, thousands of particles need a nucleation site to build the thin film

which forms layers at a substrate. This growth of nucleation onto this substrate called heterogeneous nucleation. Finally, the nuclei start to grow upwards throughout the thin film. The manner in which sputtered atoms migrate, interact and nucleate on the substrate surface is a function of many deposition process parameters; such as, sputtering power, sputtering gas, voltage, background pressure, and deposition time. Essentially, in YSZTF the appearance of oxygen vacancy from the charge balance reaction promotes the space charge region with an elevated defects concentration at the interfaces. Therefore, the anion-cation pair generation process was favorable in ion-conducting oxide heterostructure such as YSZ. Other factor related to the observed microstrain differences between S40V and S120V samples was the polycrystalline orientation of YSZ, which depended directly on the excess concentrations of sputtered atoms (Zr, Y and O). Briefly, S120V film revealing most dense structure, high polycrystallinity and moderate microstrain could be useful for SOFC electrolyte.

#### 3.3 AFM Images

Table 2 depicts the bias voltage-dependent surface roughness and standard deviation (STDV) of YSZTFs estimated from AFM topographic images, which were remarkably reduced with the increase in bias voltages except for the annealed film. In addition, results revealed that the mean grain size measured varied from 98 nm to 121 nm. Zhao et al. [37] produced YSZTFs using RF magnetron sputtering and reported comparable surface roughness values in range of 1.1 to 1.7 nm. The achievement of lowest surface roughness for S120V-600C was ascribed to the high temperature annealing assisted compactness of atoms within the grains, less lattice mismatch and well dispersion of grains on the entire substrate surface, which was consistent with lattice microstrain analysis. The wide variation in the STDV values was due to the structural non-uniformity aroused from porous columnar boundaries, which

was supported by the GAXRD data showing predominantly amorphous morphology (lack of lattice orientations).

Figure 5 presents the 3D AFM topographic images and corresponding grain size distribution of the studied YSZTFs. The influence of varied bias voltages was clearly seen in the evolving morphology, films uniformity, improved crystallinity and narrowing down in the grain size distribution. Such effect of bias voltage variations on the overall structure and morphology of YSZTFs were also reported by Tolstova et al. [21]. It was argued that with increasing substrate voltages the density of voids was reduced due to intense growth of dense columnar and fibrous grain boundaries. The appreciable decrease in the surface roughness values at 120 V was majorly ascribed to the structural transition where atomic arrangements became more compact by minimizing the thermodynamic free energy of the film. The lower surface roughness at higher voltages (especially for S120V-600C) could be due to the filling up of voids by surface diffusion of high energetic bombarded atoms, which in turn enhanced the columnar growth with tight grain boundaries. Furthermore, high polycrystallinity of the films led to fewer dislocations. Generally, for YSZTFs (8 mol% of Y<sub>2</sub>O<sub>3</sub>) 3D growth mode is reasonable because the aspect ratios of grain are close to one other [38]. According to Jonhoo et al. [39], moderate surface roughness and homogenous grain size distribution of YSZTFs could provide available reaction sites per unit of electrolyte and electrode advantageous for SOFC implementation.

#### 3.4 EDX Spectra

Figure 6 shows the cross-sectional FESEM images and the corresponding EDX spectra of studied YSZTFs. EDX analysis revealed the correct elemental compositions of the synthesized films. The detected weight percent of zirconium, yttrium and oxygen in the YSZTFs were appropriate as displayed in Figure 7.

The amounts of Zr (65.6 wt%), O (8.5 wt%) and Y (4.5 wt%) in S120V-600C were higher than the one detected in S0V sample despite of low thickness. The occurrence of such higher elemental percentages was attributed to the homogeneity and uniformity of the prepared thin film in the absence of any boundary between film and substrate. Actually, at higher bias voltage the diffusivity of atom bombardment in the layer of YSZ was enhanced, thus increased the amount of chemical species (Zr and Y with less O) in the film. The results clearly showed that the Zr and Y elements were distributed uniformly on the surface of the glass support without high differences indicated the homogeneity of element distribution by using sputtering technique.

#### 3.5 Raman Spectra

Figure 8 illustrates the room temperature Raman spectra of the as-deposited YSZTFs in the wavenumber range of 100 to 800 cm<sup>-1</sup>, which consisted of three significant bands positioned in the range of 107 to a 109 cm<sup>-1</sup> (weak), 141 to 142 cm<sup>-1</sup> (intense) and 476 to 491 cm<sup>-1</sup> (broad) accompanied by band frequency shift and broadening. This observed shift in the band position and broadening with the increse of biad voltage and annealing was attributed to the effect of mode softening associated with the shrinkage of grain (quantum confinement), presence of oxygen vacancies, and phonon confinement. Recently. similar observation was made by Jaffari et al. [40]. According to Jung et al. [41] the appearance of the broad band in the range of 470-475 cm<sup>-1</sup> could be assigned to tetragonal phase of YSZ. In our opnion, there could be a possibility of cubic to tetragonal phase transformation in the YSZTFs induced by bias voltage and subsequent annealing. Besides, the effect of compressive stress may be responsible for such band broadening accompanied by a shift [42].

Figure 9(a-d) compares the Raman bands positions and assignments of the studied YSZTFs with others reported in the literature. After systematic convolution of the spectral

data the characteristic bands were classified as strong (s), medium (m), weak (w), broad (b) and shoulder (sh). Electronic polarization active vibration modes were observed and bands in the Raman spectra [43]. It is known that the monoclinic crystal phase of  $ZrO_2$  encloses four molecules per unit cell with 27 Raman active modes ( $9_{Ag}$ ,  $9_{Cg}$ , and  $9_{Bg}$ ). The tetragonal  $ZrO_2$ contains two molecules per unit cell with 7 Raman active modes ( $A_{1g}$ , C, 2B1g, and 3Eg). The cubic zirconia with a fluorite structure has four molecules per unit cell wich reveals only one Raman active mode ( $F_2$ ) [43]. In the present study, all the significant bands were fully indexed and agreed with those reported in the literature [44,45]. However, some of the extremely weak bands could not be assigned to the appropriate bonding vibration, thus remained undefined. Refinment of the peak around 100-267 cm<sup>-1</sup> clearly revealed the  $O_{II}$ -Zr- $O_{II}$  stretching mode of YSZTFs. The intensity of stretching mode corresponding to the tetragonal phase were weakened in S40V. The enhanced peak at 271.487 cm<sup>-1</sup> for S120V-600C film indicated the presence of lower symmetry with increasing fraction of tetragonal phase, where the oxygen induced dislocations was responsible to the elongation of crystallographic c-axis and shortening of the a-axis after annealing at 600 °C [38,45].

The intensity of  $B_{1g}$  mode for 120V-600C is too weak. Moreover, the  $B_{1g}$  coupled Zr-O bending and stretching modes slighty shifted as the bias voltage was increased from 40 V to 120 V, indicating some structural disorder due to increasing contents of Y<sup>3+</sup>doping. This observation was consistent with other findings [43,45]. The peak position for Zr-O stretching mode was shifted towards higher wavenumber with increasing bias voltage, which was attributed to change in polarizability during the excitation of Raman active mode. The bond length of Zr-O was symmetrically reduced, increasing the lattice vibration energy and the wavenumber. Structural analysis of S40V sample also confirmed the existence of large lattice microstrain compared to S120V and S120V-600C, which was majorly ascribed to the oxygen displacement in the phase mixture of cubic and tetragonal zirconia. Conversely, the

elongation of Zr-O bond length was attributed to the electronegativity of metal and decrease in the force constant as well as the wavenumber [46].

The A<sub>1g</sub> modes for O-Zr-O symmetric stretching (603 cm<sup>-1</sup>) was associated to the cubic structure [29, 30]. Raman spectra revealed peak of t-YSZ type vibration. Cubic to tetragonal phase transition in doped zirconia occured via both enlargement of one of the crystallographic axes and distortion of oxygen from ideal position in fluorite structure [47]. The triply degenerate  $F_{2g}$  mode (465 cm<sup>-1</sup>) was not observed (Figure 9) because of its IR active nature. The space group of stable YSZ (8 mol% of Y<sub>2</sub>O<sub>3</sub>) belong to Fm3m point group with cubic fluorite type structure, which reveals six optical-phonon brances and yeilds three zone-center frequencies. In the proposed YSZTFs one of this observed mode around 619 cm<sup>-1</sup> was allocated to the  $F_{2g}$  symmetric O-Zr-O stretching mode of micro-crystalline YSZ (cubic phase). This in turn confirmed the presence of  $F_{2g} + (c-YSZ) + A_{1g}$  and  $E_g$  (t-YSZ) in S120V-600C as reported previously [45,49]. Furthermore, the observed increase in the wavenumber was attributed to the oxygen vacancies mediated long range order in the anion sublattice or to stable trasformation with more complex phases of lower symmetry. Such effects were authenticated by examining the sensitivity of Raman spectra towards oxygen ions polarizability and symmetry change of YSZ [47].

The red shift (from 641.879 to 635.272 cm<sup>-1</sup>) of the asymmetric O-Zr-O stretching mode ( $E_g$  from 640 cm<sup>-1</sup>) for S120V-600C film was attributed to the reduction of the lattice compressive strain of the lattice due to annealing. This reduced compressive strain led to the coalescence of smaller crystallites allowed the growth of larger grain with high crystallinity [50,51]. Using the asymmetric brodening and red shift of Raman band, Jaffari et al. [40] estimated the crystal size and inhomogeneous strain. Furthermore, the Raman spectra of all samples displayed the weak band corresponding the monoclinic (177 cm<sup>-1</sup>) and tetragonal (260 cm<sup>-1</sup>) structure. Thirupathy et al. [52] also observed a prominant Raman peak around

147.18 cm<sup>-1</sup>, assigned to the tetragonal phase of YSZ (t-YSZ). This result suggested that the symmetrical stretching vibration involving the tetragonal and cubic pahse of zirconia was sensitive to the substrate bias voltage variation which generated defects and oxygen vacancies. Meanwhile, thermal effects altered the crystal size and led to the creation of microstrain and shift in the vibrational peak position. In addition, it was shown that structural evolutions in S120V-600C film could cause higher crystallinity (large grains) and more intense Raman peaks compared to other samples.

#### 3.6. Fourier-transform Infrared Spectra

Figure 10 illustrates the room temperature FTIR specta of the studied YSZTFs in the mid-infrared region ( $600 - 400 \text{ cm}^{-1}$ ). Table 3 summarizes the FTIR band positions and assignments. FTIR band corresponding to the ZrO<sub>2</sub> functional unit together with stretching vibration of symmetric metal oxide (M-O) bond of Zr(Y)-O at around 450 – 550 cm<sup>-1</sup> were evidenced, which was supported by other report [55]. Presence of weak M-O bands at 447, 485, 504, 523 and 532 for S0V, S40V and S120V films indicates their less phase transformation. The observed intense transmission bands for S120V-600C film clearly suggested the annealing temperature assisted strong phase transformation. Such phase conversion could reduce the compressive residual strain development and thus enhanced the ionic conductivity of YSZTFs [56,57].

The FTIR band occurred at 465 cm<sup>-1</sup> for S120V and S120V-600C films was allocated to the  $F_{2g}$  mode of their cubic structure. Present observation is different from the other report on YSZTF containing 8 mol% of Y<sub>2</sub>O<sub>3</sub> [58,59]. The appearance of FTIR band shift in the region of 463 to 465 cm<sup>-1</sup> for S120V film was attributed to the oxygen stretching vibrations in the M-O linkages, which suggested the presence of fluorite-structure (metal dioxides) because the amount of Zr bonded to the O was very high. Conversely, S120V-600C did not show any

shift in the transmittance bands. The only allowed Raman mode ( $F_{2g}$ ) was viewed as a symmetric breathing mode of the O atoms around each cation [17]. The phonon vibration mode for  $ZrO_2$  unit was appeared at 480 and 560 cm<sup>-1</sup> [60]. Both S120V and S120V-600C films divulged intense IR bands at 417 cm<sup>-1</sup> assigned to Zr-O sttetching vibration, in which the absorption intensity was increased due to annealing at 600 °C. The presence of a weak band at 416 cm<sup>-1</sup> for S0V and S40V films strongly indicated the presence of elongated and weak Zr-O bonds with sluggish stretching vibration.

The occurrences of weak bands at around 422 to 423  $\text{cm}^{-1}$ , 447  $\text{cm}^{-1}$  and 516 to 523 cm<sup>-1</sup> for S120V film was ascribed to the varied crystal structure in the evolved morphology. This observation indeed supported the earlier argument where two kinds of structures could have co-existed in the YSZTFs due to low and high substrate bias voltage and post annealing. The weakening in the stretching vibration with increasing Zr content was attributed to the higher atomic weight (91.224 g/mol) and lower ionic radius (0.84 Å for Zr<sup>4+</sup>) of Zr than Y (atomic weight of 88.906 g/mol and 1.019 Å for  $Y^{3+}$ ). Substitution of Zr by Y could elongate and shorten the bond spacing around Y and Zr atoms, respectively [61]. Furthermore, an enhancement in the nanocrystalline density (smaller crystallite size) could increase the refractive index and thus the transmittance of the studied films. Generally, the transmittance of the YSZTF is very low due to wide optical band gap. Moreover, this enhanced transmittance was responsible for the alterations in the molecular vibration (Table 4), which may be promising for improving the ionic conductivity of YSZTFs. It was asserted that the variation in the RF bias voltage could selectively bombard the high energetic ions onto the substrate to create unique film morphology effective for SOFC electrolyte applications [12]. These bombarded ions could remove the loosely bonded atoms from the substrate surface and reduced the degree of contamination (defects, pores, inhomogeneity and dislocations) in the deposited YSZTFs.

#### 4.0 Conclusion

We examined the structure and morphology evolution of YSZTFs as a function of substrate bias voltages and annealing temperature. These films were grown using radio frequency magnetron sputtering technique. Film annealed at 600 °C revealed improved structures and morphology. Highly polycrystalline film (cubic symmetry) without any impurities was achieved. The attained microstructures could be ideal for high oxide ion conductivity required for SOFC electrolytes. Film prepared at 120 V exhibited dense noncolumnar structure with least microstrain and co-existence of two crystal phases. These films showed dense morphology with small crystallite sizes. The YSZTF prepared at bias voltage of 120 V with 600 °C annealing displayed highest elemental traces (Zr, Y and O) and lowest surface roughness (1.47 nm). Raman spectra of the deposited YSZTFs showed an intense band at 488  $\text{cm}^{-1}$  and a weak band at 620  $\text{cm}^{-1}$  assigned to Zr-O stretching vibrations. FTIR spectra of YSZTFs (S120V and S120V-600C) divulged intermediate broad bands around 465 cm<sup>-1</sup>, which were also allocated to Zr-O vibrations. The transmittance of the films was improved with increasing bias voltage. It was established that the structure and morphology of YSZTFs can be controlled by adjusting the substrate bias voltages and annealing temperature, wherein such films may be beneficial as electrolyte for low temperature SOFC operation.

#### ACKNOWLEDGMENT

This research work has supported by the Malaysian Ministry of Education (MOHE) through the Nanomite Programme (LRGS 4L825) and Research University Grant (GUP 16H23,

18H68, and 17H19). The authors gratefully acknowledge the MyBrain Programme (MOHE) for the financial support to Nurhamizah through partial support for PhD studies.

- J. Jiang, J.L. Hertz, On the variability of reported ionic conductivity in nanoscale YSZ thin films, J. Electroceramics. 32 (2014) 37–46.
- [2] A. Chroneos, B. Yildiz, A. Tarancón, D. Parfitt, J.A. Kilner, Oxygen diffusion in solid oxide fuel cell cathode and electrolyte materials: mechanistic insights from atomistic simulations, Energy Environ. Sci. 4 (2011) 2774.
- [3] R. Muchakayala, S. Song, S. Gao, X. Wang, Y. Fan, Structure and ion transport in an ethylene carbonate-modi fi ed biodegradable gel polymer electrolyte, Polym. Test. 58 (2017) 116–125.
- [4] T. Mukai, T. Fujita, S. Tsukui, K. Yoshida, M. Adachi, K.C. Goretta, Effect of rate on pulsed laser deposition of yttria-stabilized zirconia electrolyte thin films for SOFCs, J.
   Fuel Cell Sci. Technol. 12 (2015) 31002.
- T. Kariya, H. Tanaka, T. Hirono, T. Kuse, K. Yanagimoto, K. Uchiyama, M. Henmi,
   M. Hirose, I. Kimura, K. Suu, H. Funakubo, Development of a novel cell structure for
   low-temperature SOFC using porous stainless steel support combined with hydrogen
   permeable Pd layer and thin film proton conductor, J. Alloys Compd. 654 (2016) 171–
   175.
- [6] I. Chang, J. Bae, J. Park, S. Lee, M. Ban, T. Park, Y.H. Lee, H.H. Song, Y.B. Kim, S.W. Cha, A thermally self-sustaining solid oxide fuel cell system at ultra-low operating temperature (319 °C), Energy. 104 (2016) 107–113.
- [7] H. Jung, K. Bae, D.Y. Jang, Y.H. Lee, S.W. Cha, J.H. Shim, Evaluation of porous platinum, nickel, and lanthanum strontium cobaltite as electrode materials for lowtemperature solid oxide fuel cells, Int. J. Hydrogen Energy. 39 (2014) 17828–17835.

- [8] F. Smeacetto, M. Salvo, L.C. Ajitdoss, S. Perero, T. Moskalewicz, S. Boldrini, L.
   Doubova, M. Ferraris, Yttria-stabilized zirconia thin film electrolyte produced by RF
   sputtering for solid oxide fuel cell applications, Mater. Lett. 64 (2010) 2450–2453.
- [9] J. Nielsen, J. Hjelm, Impedance of SOFC electrodes: A review and a comprehensive case study on the impedance of LSM:YSZ cathodes, Electrochim. Acta. 115 (2014) 31–45.
- [10] J. Jiang, X. Hu, N. Ye, J.L. Hertz, Microstructure and ionic conductivity of yttriastabilized zirconia thin films deposited on MgO, J. Am. Ceram. Soc. 97 (2014) 1131– 1136.
- [11] L. Yao, G. Ou, H. Nishijima, W. Pan, Enhanced conductivity of (110)-textured ScSZ films tuned by an amorphous alumina interlayer, Phys. Chem. Chem. Phys. 17 (2015) 23034–23040.
- [12] A.R. Noviyanti, F.S. Irwansyah, S. Hidayat, A. Hardian, D.G. Syarif, Y.B. Yuliyati, I. Hastiawan, Preparation and conductivity of composite apatite La9.33Si6O26(LSO)-Zr0.85Y0.15O1.925(YSZ), AIP Conf. Proc. 1712 (2016) 0–6.
- [13] N.S. Sochugov, A.A. Soloviev, A. V Shipilova, S. V Rabotkin, V.P. Rotshtein, I.T. Sigfusson, The effect of pulsed electron beam pretreatment of magnetron sputtered ZrO 2 : Y 2 O 3 fi lms on the performance of IT-SOFC, Solid State Ionics. 231 (2013) 11–17.
- [14] A.P. Kulkarni, S. Giddey, S.P.S. Badwal, Enhancing Oxygen Reduction Reactions in Solid Oxide Fuel Cells with Ultrathin Nanofilm Electrode–Electrolyte Interfacial Layers, J. Phys. Chem. C. 120 (2016) 15675–15683.
- [15] G. Jose La O, J. Hertz, H. Tuller, Y. Shao-Horn, Microstructural features of RF-sputtered SOFC anode and electrolyte materials, J. Electroceramics. 13 (2004) 691–695.

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- [16] H. Wang, W. Ji, L. Zhang, Y. Gong, B. Xie, Y. Jiang, Y. Song, Preparation of YSZ films by magnetron sputtering for anode-supported SOFC, Solid State Ionics. 192 (2011) 413–418.
- [17] A.A. Solovyev, A. V. Shipilova, I. V. Ionov, A.N. Kovalchuk, S. V. Rabotkin, V.O.
   Oskirko, Magnetron-sputtered YSZ and CGO electrolytes for SOFC, J. Electron.
   Mater. 45 (2016) 3921–3928.
- K.S. Jeong, J. Song, D. Lim, M.S. Lee, H. Kim, M.H. Cho, Structural evolution and defect control of yttrium-doped ZrO<sub>2</sub> films grown by a sol-gel method, Appl. Surf. Sci. 320 (2014) 128–137.
- [19] S. Ji, J. An, D.Y. Jang, Y. Jee, J.H. Shim, S.W. Cha, On the reduced electrical conductivity of radio-frequency sputtered doped ceria thin film by elevating the substrate temperature, Curr. Appl. Phys. 16 (2016) 324–328.
- [20] D.E. Ruddell, B.R. Stoner, J.Y. Thompson, Effect of deposition interruption and substrate bias on the structure of sputter-deposited yttria-stabilized zirconia thin films, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 20 (2002) 1744.
- [21] Y. Tolstova, S.T. Omelchenko, A.M. Shing, H.A. Atwater, Heteroepitaxial growth of Pt and Au thin films on MgO single crystals by bias-assisted sputtering, Nat. Publ. Gr. (2016) 4–9.
- [22] B.G. Priyadarshini, S. Aich, M. Chakraborty, Substrate bias voltage and deposition temperature dependence on properties of rf-magnetron sputtered titanium films on silicon (100), 37 (2014) 1691–1700.
- [23] F. Fleischhauer, A. Tiefenauer, T. Graule, R. Danzer, A. Mai, J. Kuebler, Failure analysis of electrolyte-supported solid oxide fuel cells, 258 (2014) 382–390.
- [24] F. Fleischhauer, R. Bermejo, R. Danzer, A. Mai, T. Graule, J. Kuebler, Strength of an electrolyte supported solid oxide fuel cell, 297 (2015) 158–167.

- [25] F. Band, O. Christensen, RF biasing through capacitive collector to target coupling in RF diode sputtering, (1972).
- [26] S.H. Seo, J.H. In, H.Y. Chang, Effects of a sheath boundary on electron energy distribution in Ar/He dc magnetron discharges, J. Appl. Phys. 96 (2004) 57–64.
- [27] S. Sonderby, A.J. Nielsen, B.H. Christensen, K.P. Almtoft, J. Lu, J. Jensen, L.P. Nielsen, P. Eklund, Surface & Coatings Technology Reactive magnetron sputtering of uniform yttria-stabilized zirconia coatings in an industrial setup Zr/Y targets, 206 (2012) 4126–4131.
- [28] M. Sillassen, P. Eklund, M. Sridharan, N. Pryds, N. Bonanos, J. Bottiger, Ionic conductivity and thermal stability of magnetron-sputtered nanocrystalline yttriastabilized zirconia, J. Appl. Phys. 105 (2009).
- [29] J. Li, N. Zhang, Z. He, K. Sun, Z. Wu, Preparation and characterization of onedimensional nano-structured composite cathodes for solid oxide fuel cells, J. Alloys Compd. 663 (2015) 664–671.
- [30] I.H. Jung, K.K. Bae, K.C. Song, M.S. Yang, S.K. Ihm, Columnar grain growth of yttria-stabilized-zirconia in inductively coupled plasma spraying, J. Therm. Spray Technol. 13 (2004) 544–553.
- [31] Z.M. Rosli, K.W. Loon, J.M. Juoi, N. Nayan, Z.B. Mahamud, Y. Yusuf,
   Characterization of TiAlBN Nanocomposite Coating Deposited via Radio Frequency
   Magnetron Sputtering Using Single Hot-Pressed Target, Adv. Mater. Res. 626 (2012)
   298–301.
- [32] R. Nedelec, S. Uhlenbruck, D. Sebold, V.A.C. Haanappel, H.P. Buchkremer, D. Stöver, Dense yttria-stabilised zirconia electrolyte layers for SOFC by reactive magnetron sputtering, J. Power Sources. 205 (2012) 157–163.
- [33] S. Hong, D. Lee, Y. Lim, J. Bae, Y.B. Kim, Yttria-stabilized zirconia thin films with

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restrained columnar grains for oxygen ion conducting electrolytes, Ceram. Int. 42 (2016) 16703–16709.

- [34] S. Sprio, S. Guicciardi, a. Bellosi, G. Pezzotti, Yttria-stabilized zirconia films grown by radiofrequency magnetron sputtering: Structure, properties and residual stresses, Surf. Coatings Technol. 200 (2006) 4579–4585.
- [35] A. Kushima, B. Yildiz, Oxygen ion diffusivity in strained yttria stabilized zirconia: where is the fastest strain?, J. Mater. Chem. 20 (2010) 4809.
- [36] E. Fabbri, D. Pergolesi, E. Traversa, Ionic conductivity in oxide heterostructures: The role of interfaces, Sci. Technol. Adv. Mater. 11 (2010).
- [37] X. Zhao, J. Jin, J.C. Cheng, J.W. Lee, K.H. Wu, K.C. Lin, J.R. Tsai, K.C. Liu, Structural and optical properties of zirconia thin films deposited by reactive high-power impulse magnetron sputtering, Thin Solid Films. 570 (2014) 404–411.
- [38] D. Stender, R. Frison, K. Conder, J.L.M. Rupp, B. Scherrer, J.M. Martynczuk, L.J. Gauckler, C.W. Schneider, T. Lippert, A. Wokaun, Crystallization of zirconia based thin films, Phys. Chem. Chem. Phys. 17 (2015) 18613–18620.
- [39] J. Park, Y. Lee, I. Chang, G. Young, S. Ji, W. Lee, S. Won, Atomic layer deposition of yttria-stabilized zirconia thin fi lms for enhanced reactivity and stability of solid oxide fuel cells, 116 (2016) 170–176.
- [40] G.H. Jaffari, A. Imran, M. Bah, A. Ali, A.S. Bhatti, U. Saeed, S.I. Shah, Applied Surface Science Identification and quantification of oxygen vacancies in CeO<sub>2</sub> nanocrystals and their role in formation of F-centers, Appl. Surf. Sci. 396 (2017) 547– 553.
- [41] W. Jung, J.L. Hertz, H.L. Tuller, Enhanced ionic conductivity and phase meta-stability of nano-sized thin film yttria-doped zirconia (YDZ), 57 (2009) 1399–1404.
- [42] L. Kurpaska, M. Frelek-Kozak, K. Nowakowska-Langier, M. Lesniak, J. Jasinski, J.

Jagielski, Structural and mechanical properties of Ar-ion irradiated YSZ single-crystals grown in different crystallographic orientations, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 409 (2017) 81–85.

- [43] A.P. Naumenko, N.I. Berezovska, M.M. Biliy, O. V Shevchenko, Vibrational analysis and raman spectra of tetragonal zirconia, 1 (2008) 121–125.
- [44] S. Heiroth, T. Lippert, A. Wokaun, M. Döbeli, J.L.M. Rupp, B. Scherrer, L.J.
   Gauckler, Yttria-stabilized zirconia thin films by pulsed laser deposition :
   Microstructural and compositional control, 30 (2010) 489–495.
- [45] S. Heiroth, R. Frison, J.L.M. Rupp, T. Lippert, E.J. Barthazy, E. Müller, M. Dobeli, K. Conder, A. Wokaun, L.J. Gauckler, Crystallization and grain growth characteristics of yttria-stabilized zirconia thin fi lms grown by pulsed laser deposition, 191 (2011) 12–23.
- [46] L. Qu, K. Choy, R. Wheatley, Theoretical and experimental studies of doping effects on thermodynamic properties of (Dy,Y)-ZrO<sub>2</sub>, Acta Mater. (2016) 7–14.
- [47] A. Maghsoudipour, L.M. Gorjani, F. Hashemzadeh, Synthesis and characterization of cubic yttria-stabilized zirconia (8YSZ) nanoparticles by a modified sol-gel route using sucrose and pectin as organic precursors, 6 (2011) 2518–2525.
- [48] H.P. Dasari, J.S. Ahn, K. Ahn, S. Park, J. Hong, H. Kim, K.J. Yoon, J. Son, H. Lee, J. Lee, Synthesis, sintering and conductivity behavior of ceria-doped Scandia-stabilized zirconia, Solid State Ionics. 263 (2014) 103–109.
- [49] S. Heiroth, T. Lippert, A. Wokaun, M. Döbeli, J.L.M. Rupp, B. Scherrer, L.J.
   Gauckler, Yttria-stabilized zirconia thin films by pulsed laser deposition:
   Microstructural and compositional control, J. Eur. Ceram. Soc. 30 (2010) 489–495.
- [50] C. Ko, K. Kerman, S. Ramanathan, Ultra-thin film solid oxide fuel cells utilizing undoped nanostructured zirconia electrolytes, J. Power Sources. 213 (2012) 343–349.

[51]	S. Akasaka, Thin film YSZ-based limiting current-type oxygen and humidity sensor on
	thermally oxidized silicon substrates, Sensors Actuators, B Chem. 236 (2016) 499-505.
[52]	T. Maridurai, D. Balaji, S. Sagadevan, Synthesis and characterization of yttrium
	stabilized zirconia nanoparticles, Mat. Res. 19 (2016) 812-816.
[53]	M. Hajizadeh-Oghaz, R. Shoja Razavi, M.R. Loghman-Estarki, Synthesis and
	characterization of non-transformable tetragonal YSZ nanopowder by means of Pechini
	method for thermal barrier coatings (TBCs) applications, J. Sol-Gel Sci. Technol. 70
	(2014) 6–13.
[54]	E. Djurado, F. Boulc'h, L. Dessemond, N. Rosman, M. Mermoux, Study on Aging of
	Tetragonal Zirconia by Coupling Impedance and Raman Spectroscopies in Water
	Vapor Atmosphere, J. Electrochem. Soc. 151 (2004) A774.
[55]	I. Kaus, P.I. Dahl, J. Mastin, T. Grande, M. Einarsrud, Synthesis and Characterization
	of Nanocrystalline YSZ Powder by Smoldering Combustion Synthesis, 2006 (2006) 1-
	7.
[56]	B. Bagchi, R.N. Basu, A simple sol-gel approach to synthesize nanocrystalline 8 mol%
	yttria stabilized zirconia from metal-chelate precursors: Microstructural evolution and
	conductivity studies, J. Alloys Compd. 647 (2015) 620-626.
[57]	T.H. Yeh, R. De Lin, J.S. Cherng, Significantly enhanced ionic conductivity of yttria-
	stabilized zirconia polycrystalline nano-film by thermal annealing, Thin Solid Films.
	544 (2013) 148–151.
[58]	S.S. Chopade, C. Nayak, D. Bhattacharyya, S.N. Jha, R.B. Tokas, N.K. Sahoo, M.N.
	Deo, a. Biswas, S. Rai, K.H. Thulasi Raman, G.M. Rao, N. Kumar, D.S. Patil, RF
	plasma enhanced MOCVD of yttria stabilized zirconia thin films using octanedionate
	precursors and their characterization, Appl. Surf. Sci. 355 (2015) 82-92.
[59]	D. Das, B. Bagchi, R.N. Basu, Nanostructured zirconia thin fi lm fabricated by

electrophoretic deposition technique, J. Alloys Compd. 693 (2017) 1220–1230.

- [60] N. Duan, H. Lin, L. Li, J. Hu, L. Bi, H. Lu, J. Xie, L. Deng, ZrO 2 -TiO 2 thin films : a new material system for mid-infrared integrated photonics, Opt. Mater. Express. 3 (2013) 154–159.
- [61] S.S. Chopade, C. Nayak, D. Bhattacharyya, S.N. Jha, R.B. Tokas, N.K. Sahoo, M.N. Deo, A. Biswas, S. Rai, K.H.T. Raman, G.M. Rao, N. Kumar, D.S. Patil, Applied Surface Science RF plasma enhanced MOCVD of yttria stabilized zirconia thin films using octanedionate precursors and their characterization, Appl. Surf. Sci. 355 (2015) 82–92.

#### **Figure captions**

Figure 1: FESEM images of all YSZTFs with (a-d) top-view, and (A-D) cross-sectional view.

Figure 2: GAXRD pattern of studied YSZTFs

**Figure 3:** Refinement of GAXRD pattern fitted to Gaussian (solid curve) for the four major peaks (a) [111], (b) [200], (c) [220] and (d) [311].

Figure 4: Lattice microstrain along four significant crystal lattice orientations.

**Figure 5:** AFM images and corresponding grain size distribution of (a-A) S0V, (b-B) S40V, (c-C) S120V, and (d-D) S120V-600C.

**Figure 6:** Cross-sectional FESEM images showing scanned area (rectangular box) and the corersponding EDX spectra of YSZTFs (a-A) S0V, (b-B) S40V, (c-C) S120V, and (d-D) S120V-600C.

Figure 7: Detected elements (wt%) in the YSZTFs obtained using EDX spectral analysis.

Figure 8: Raman spectra of studied YSZTFs.

**Figure 9:** Raman band position and assignments compared to other reports for the studied YSZTFs (a) S0V, (b) S40V, (c) S120V, and (d) S120V-600C. The symbols in the table indicate the nature of the bands with sh for shoulder, w for weak, m for medium, b for broad, and s for strong.

# Figure 10: FTIR spectra of the studied YSZTFs

 Table 1: Average thickness of the studied YSZTFs.

**Table 2**: Bias voltage dependent surface roughness, standard deviation and grain size ofYSZTFs.

Table 3: FITR band positions and assignments for studies YSZTFs compared to other reports.





Figure 1:



Figure 2:



Figure 3:



Figure 4:



Figure 5:



Figure 6:



Figure 7:



Figure 8:









**Figure 9:** Raman band position and assignments compared to other reports for the studied YSZTFs (a) S0V, (b) S40V, (c) S120V, and (d) S120V-600C. The symbols in the table indicate the nature of the bands with sh for shoulder, w for weak, m for medium, b for broad, and s for strong.



Figure 10:

Sample Code Mean		Mean Crystallite	Microstrain (%) along	
	Thickness	Size (nm)	different direction	
	(nm)			
SOV	196.6	-	-	
S40V	225.2	19.92	0.427	
S120V	S120V 115.4		0.311	
S120V-600C	208.4	17.78	0.296	

#### Table 1:

Table 2:

Sample Code	Surface roughness (nm)	STDV (nm)	Mean grain size (nm)
SOV	8.44	40.590	-
S40V	4.25	23.573	98.092
S120V	3.18	19.327	107.905
S120V-600C	1.47	26.493	121.3594

#### Table 3:

	Band position (cm <sup>-1</sup> ) for YSZTFs			Ref.	
Band assignments	SOV	S40V	S120V	S120V-600C	
Stretching of the Zr(Y)-O	407	404	407	-	
bonds (Intense bands)	416	416	417	417	419 [61]
	422	422	-	423	Present
					work
Stretching of the Zr(Y)-O	427	428	431	435	This work
bonds (Intermediate broad adsorption)	439	436	439	440	This work
	447	447	-	447	This work
	464	463	465	465	This work
Stretching of the Zr(Y)-O	455	-	455	455	458 [61]
bonds (Strong broad					
adsorption)					
	-	-	-	485	480 [60]
	-	-	-	504	504 [61]
Stretching of the Zr(Y)-O	516	519	-	523	This work
bonds (Weak shoulder)	-	-	-	532	594,
					632,636
					[61]