Thermal Expansion, Phase stability and Interdiffusion in Pulsed laser Deposited Multilayers of ZrO_2/Y_2O_3

P. Kuppusami [1*], Maneesha Mishra [2]

[1]Centre for Nanoscience and Nanotechnology, Centre of Excellence for Energy Research, Sathyabama University, Chennai-600119, Tamil Nadu, India.

[2] Center for Interdisciplinary Molecular Science, National Chiao Tung University, 1001 Univ. Road, Hsinchu 300, Taiwan

Abstract

The present study reports the thermal expansion behavior of multilayer films of ZrO_2/Y_2O_3 deposited on Si (100) substrates by pulsed laser deposition. Multilayers were deposited with different ZrO_2 layer thickness varying from 5 to 30 nm and Y_2O_3 layer with constant thickness of 10 nm. The multilayers were subjected to two stage heat treatment in high temperature X-ray diffraction equipment, in the temperature range 300-1373 K. Coefficient of thermal expansion of tetragonal zirconia and the effect of ZrO_2 layer thickness on stability of multilayer structure are explained on the basis of solubility, ionic size and inter-diffusion effects.

Keywords: *Thermal expansion, X-ray diffraction, Multilayers, Zirconia, Yttria*

1. Introduction

Evaluation of coefficient of thermal expansion (CTE) of films is an important parameter to choose a material for different applications such as solid oxide fuel cells (SOFC), thermal barrier coatings (TBC), microelectronics and micromechanical systems. The common techniques that are being used to measure the CTE values for bulk materials are mechanical dilatometry [1], optical interferometry [2] and diffraction techniques [3]. In case of the thin film structures, these methods cannot be used because of lack of accuracy in the measurements due to smaller thickness. Measurement of the CTE values of a thin film can be carried out by high temperature X-Ray diffraction (HTXRD) [4], ellipsometer [5] and micromachined cantilever techniques [6]. Among these techniques, HTXRD finds its importance in determination of CTE values due to the advantages such as (i) smaller size (nanometre length scale and low volume fraction of the newly formed phases) of sample (ii) simultaneous measurement of CTE of different phases due to phase transformation, and (iii) the expansion along different crystallographic directions can also be determined. Since the unit cell size of the crystalline solid changes with temperature due to anharmonic component in lattice vibrations, HTXRD is suitable only for crystalline films. However, HTXRD can be used to study the thermal stability, phase evolution as well as inter-diffusion occurring during the heat treatment. Other methods like dilatometry requires specimen compacted to near theoretical density in order to obtain reliable values.

Multilayers are composed of two different alternating layers of metals, nitrides, carbides or oxides. In the 20 years, several nitride multilayers with different thermal stability have been reported [7,8]. It has been recommended that for high thermal stability, the material structure must exhibit stable thermodynamic behaviour and form interfaces of high coherent strength [9]. Multilayers with coherent low energy interfaces are isostructural materials such as Cu/Ni and TiN/ NbN and they undergo inter-diffusion at elevated temperatures [9]. Balakrishnan et al. [10,11] have

analyzed the thermal stability and thermal expansion behaviour of ZrO_2/Al_2O_3 and CeO_2/ZrO_2 multilayer films deposited by PLD technique. Barshilia et al. [12] have prepared ZrO_2/Al_2O_3 and ZrO_2/Y_2O_3 by sputtering technique and analyzed the microstructural and nanomechanical properties of the films. Maneesha et al. [13] have recently reported the thermal expansion of multilayers of ZrO_2/Y_2O_3 prepared by pulsed laser deposition (PLD) with variation in ZrO_2 layer thickness from 5 to 30 nm, while keeping Y_2O_3 layer thickness constant. The present work investigates the complexities involved in the analysis of the thermal expansion coefficients and the inter-diffusion and the thermal stability of multilayers of ZrO_2/Y_2O_3 in the above work. PLD has been used in the present study because of the following advantages of PLD compared to other established deposition methods: (i) capability of stoichiometric transfer of the target composition to the film, (ii) decoupling of the vacuum system and laser energy source, (iii) deposition from ambient to high vacuum, and (iv) deposition of metastable materials due to non-equilibrium conditions during laser ablation.

2. Materials and Methods

Multilayers of ZrO_2/Y_2O_3 were prepared from sintered ZrO_2 and Y_2O_3 targets by pulsed laser deposition technique. A KrF excimer laser (Lambda Physik Compex-205, 248 nm wavelength) was used with 300 mJ per pulse at a repetition rate of 10 Hz to evaporate the targets for multilayer deposition. Before the deposition of multilayers, single layers of Y_2O_3 and ZrO_2 were deposited and their deposition rates were found to be 8 nm/min and 5 nm/min. All these films were deposited on Si (100) substrates at substrate temperature of 300 K and oxygen partial pressure of 2 Pa.

The layer thickness of ZrO_2 was varied from 5 to 30 nm, whereas the Y_2O_3 layer thickness was kept at 10 nm. The total thickness of the multilayer films were kept constant by varying the bi-layer thickness. The total number of bilayers for the ZrO_2 layer thickness of 5, 10, 20, and 30 nm were 65, 50, 35 and 25, respectively The details of target preparation and the other experimental conditions for the deposition of multilayers are reported in [13].

HTXRD experiments of the single as well as multilayer samples were carried out using an INEL XRG-3000 X-ray diffractometer attached with a high temperature arrangement (Buhler HDK 2.4) at an incident angle of (ω) 5˚. Films deposited on Si (100) substrates were kept on a tantalum base and in-situ heated in the temperature range of 300 - 1373 K with a heating rate of 10 K/min and the patterns were recorded for a time period of 15 minutes and after 3 minutes of stabilization time using a curved position sensitive detector in the 2Θ range of 10º – 100º. After the measurements, the samples were cooled at a rate of 50 K/min to room temperature.

In the present study, all the multilayer films were heat treated for two times under similar conditions in the temperature range of 300-1373 K as mentioned above. The first heat treatment was carried out to relieve stress and to form a crystalline film and the second heat treatment was carried out to collect the data on lattice parameter in order to determine the thermal expansion values [14].

From the HTXRD pattern, the changes in the lattice parameter and phase stability were monitored and the lattice parameters were calculated using "unit cell" program with second order polynomial fitting [15]. From the lattice parameter data, average linear coefficient of thermal expansion (α_a) as well as instantaneous coefficient of thermal expansion (α_{inst}) values were calculated using equation 1 and 2, respectively [16].

$$\alpha_a = \frac{1}{a_{Rt}} \left[\frac{a_T - a_{Rt}}{T - RT} \right] \ K^{-1} \ \dots\dots\dots\dots\dots\dots (1)$$

$$\alpha_{inst} = \frac{1}{a_T} \left[\frac{\partial a}{\partial t} \right] \ K^{-1} \ \dots\dots\dots\dots\dots\dots (2)$$

Where α_a is the average thermal expansion coefficient along a axis, a_T and a_{RT} are the lattice parameter values at temperature T and room temperature (RT), respectively.

3. Results and Discussion

As indicated in the experimental conditions, single layers of yttria, zirconia and multilayers of ZrO_2/Y_2O_3 were first heat treated in-situ in high temperature XRD in the temperature range of 300-1373 K with the heating rate of 10 K/min and the patterns were recorded for a time period of 15 minutes and after 3 minutes of stabilization time. This treatment has reduced stress in the film and promoted crystalline films. In order to determine the CTE, these single layers and multilayers were subjected to the second heat treatment schedule under similar heat treatment conditions followed for the first heat treatment to

International Journal of Advanced Scientific Research and Management, Vol. 1 Issue 6, June 2016.

www.ijasrm.com

ISSN 2455-6378

estimate the CTE of yttria and zirconia and are reported in detail in ref [13]. The following section reports and discusses the complexities and various influencing parameters in the CTE values obtained after the second heat treatment of these films.
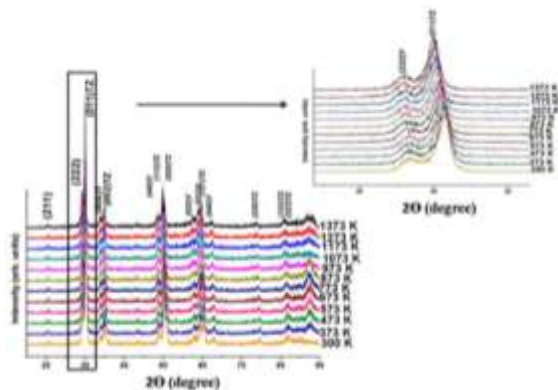

Fig. 1 HTXRD of ZrO_2/Y_2O_3 of (20/10 nm) after second heat treatment. The inset shows the enlarged view of the (222) reflection from yttria and (011) t-zirconia [13].

Figure 1 shows a typical HTXRD pattern of the (20/10) nm thick ZrO_2/Y_2O_3 multilayer subjected to the second heat-treatment in the temperature range 300-1373 K. The figure shows (211), (222), (400), (440), (622), (631) and (640) reflections of cubic yttria (c-Y_2O_3) and (011), (002), (112), (020), (121), (220), (123) and (222) reflections of tetragonal zirconia (t-ZrO_2). Unlike the single layer films of ZrO_2 having a two phase structure (monoclinic and tetragonal), ZrO_2 was stabilized in tetragonal structure when deposited on yttria for all the multilayers [13]. The cubic phase of yttria could act as a template to force a few atomic layers of zirconia to stabilize in tetragonal form as the latter phase differs slightly only along c-axis compared to that of cubic phase of zirconia. Similar observation has been reported in TiN/Cr_2N superlattice system, where the usually hexagonal Cr_2N is forced into fcc structure [17]. Also, Y_2O_3 and ZrO_2 are known to form a limited solid solution, since the solubility of ZrO_2 in Y_2O_3 is ~20 %, where as solubility of Y_2O_3 in ZrO_2 is ~50-55% as per the phase diagram of Y_2O_3 and ZrO_2 [18]. The tendency for yttria to form a limited solid solution with zirconia also changes the phase boundary and promotes the formation of tetragonal phase at low temperature. The structural similarity and higher solubility of yttria and zirconia with negligible constraint by yttria facilitates the phase stabilization of t-ZrO_2. Another reason for the phase stabilization of t-ZrO_2 is the generation of oxygen ion vacancies at higher temperatures as a consequence of doping yttria

with zirconia. To accommodate the thermally generated oxygen ion vacancies, the structure of ZrO_2 changes to either tetragonal or cubic with eight fold co-ordination [19]. In contrast, the stabilization of t-ZrO_2 was achieved with Al_2O_3 through constraint imposed by grain size [20] or by critical layer thickness as reported by Balakrishnan et al. [10,11].

The lattice parameter values for t-ZrO_2 and c-Y_2O_3 of the ZrO_2/Y_2O_3 multilayer were determined and the lattice parameter values against temperature with the second order polynomial fitting for t-ZrO_2 along a and c axis and c-Y_2O_3 are shown below:

$$c_Z(\mathring{A}) = 5.125 \times 10^{-10} + 5.81 \times 10^{-15} \times T + 1.335 \times 10^{-18} \times T^2 \dots\dots (3)$$
$$a_Z(\mathring{A}) = 3.585 \times 10^{-10} + 5.606x10^{-16} \times T + 1.826 \times 10^{-18} \times T^2 \dots\dots (4)$$
$$a_Y(\mathring{A}) = 10.502 \times 10^{-10} + 5.318x10^{-15} \times T + 1.443 \times 10^{-18} \times T^2 \dots (5)$$

Using the above equations, the average CTE values were calculated in the temperature range of 300 - 1373 K. The average CTE values of tetragonal ZrO_2 were found to vary from 4.61- 15.53 x 10^{-6} K^{-1}, and 12.85-18.42 x 10^{-6} K^{-1} along a and c-axes respectively and the variation was in the range 5.83- 8.76 x 10^{-6} K^{-1} for c-Y_2O_3. In the similar way, the CTE values of t-ZrO_2 and c-Y_2O_3 of ZrO_2 /Y_2O_3 multilayers of (30/10) nm, (10/10) and (5/10) nm thickness were determined. Since the expansion along c-axis much larger than along a-axis, the CTE values along c-axis alone is considered for t-ZrO_2 in the present study for discussion. Tables 1 and 2 list the CTE values of c-yttria and t-ZrO_2 along c-axis, respectively. From Table 1 and 2 it is clear that the CTE values increase slightly in the case of c-Y_2O_3, while there is a significant increase with temperature for t-ZrO_2.
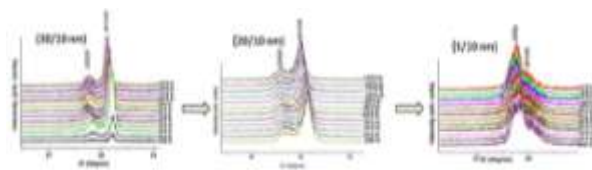

Fig. 2 Variation in HTXRD profiles of (222) of c-yttria and (011) of t-zirconia in ZrO_2/Y_2O_3 multilayers after the second heat treatment.

Fig. 2 shows the variation in the diffraction profiles of (222) of c-Y_2O_3 and (011) of t-ZrO_2 obtained for the

multilayers of ZrO_2/Y_2O_3 of (30/10) nm, (20/10) nm and (5/10) nm in the 2Θ scan range of 27º – 33º. It is clear that with the decreasing thickness of zirconia layer from 30 nm to 5 nm, there is a decreasing intensity and peak shift in the c-Y_2O_3 towards (011) t-zirconia. At zirconia layer thickness of 5 nm, there is a serious overlap of zirconia with yttria peak indicating a tendency for the dissolution of yttria in zirconia which leads to a difficulty in determining the CTE of t-zirconia with the multilayers of (5/10) nm.

Table 1: The CTE of c- Y_2O_3 of single and multilayers

Temperature (K)	CTE x10^{-6} (K^{-1}) Single layer	CTE x10^{-6} (K^{-1}) (30/10) nm	CTEx10^{-6} (K^{-1}) (20/10) nm	CTE x10^{-6} (K^{-1}) (10/10) nm	CTE x10^{-6} (K^{-1}) (5/10) nm
300	5.37	5.16	5.83	6.82	4.86
373	5.58	5.185	6.03	6.83	5.11
473	5.86	5.225	6.31	6.85	5.47
573	6.14	5.26	6.58	6.87	5.82
673	6.42	5.295	6.85	6.89	6.17
773	6.71	5.335	7.12	6.90	6.53
873	6.99	3.37	7.40	6.92	6.88
973	7.27	5.405	7.67	6.94	7.23
1073	7.55	5.445	7.94	6.96	7.58
1173	7.83	5.480	8.21	6.98	7.94
1273	8.11	5.502	8.49	7.00	8.29
1373	8.39	5.555	8.76	7.01	8.64

The inter-diffusion effects were also observed from the XRD analysis of the multilayers across the interfaces (Fig. 2). Both the intensities as well as peak positions of yttria and t- ZrO_2 change as a function of temperature and zirconia layer thickness. Tendency for zirconia to overlap with yttria is evident with the multilayer, where the thickness of zirconia is 5 nm. The ionic radii of Y^{3+} (~101 pm) [21] is greater than that of Zr^{4+} ions (~80 pm) [22] and therefore, at higher temperatures, the Y^{3+} sites are replaced by Zr^{4+} resulting in a lattice contraction [23]. The decrease in the lattice parameter values with the increase in temperature has also been reported in literature as a result of replacement of atomic lattice by relatively smaller sized ions [24]. The CTE values of t-ZrO_2 in the multilayers were found to be higher than that of the values reported for the single layer films. The reason could be the replacement of the Zr^{4+} sites by Y^{3+}. The CTE values of t-ZrO_2 in multilayers increase with decrease in ZrO_2 layer thickness which results in higher thermal expansion with increase in the

temperature than that of the single layered materials [25]. High resolution electron microscopy of the zirconia/yttria multilayer after first heat treatment schedule also showed intermixing of a few atomic layers at the interfaces[13], while in the case of alumina/ zirconia, alumina was amorphous up to the annealing temperature of 1473 K [26].

The doping of oversized cations such as Y^{3+} is found to favour eight fold co-ordination and allow association of the oxygen ion vacancies with the host Zr^{4+} cations. As a result, an increased concentration of oxygen ion vacancies associated with Zr^{4+} can be produced. Besides this, inter-diffusion can also lead to formation of oxygen vacancies [27] and cause an increase in the thermal expansion. Hayashi et al. [28] have also reported an increase in the CTE values with increase in the gadolinia content as a result of increased oxygen vacancies. Besides these factors, the decrease in zirconia layer thickness from 30 nm to 5 nm for multilayers of constant thickness also causes an increase in CTE value due to the increase in number of interfaces and increase in the total inter-diffusion area.

Temperature (K)	CTE x 10^{-6} (K^{-1}) along a-axis, Single layer	CTE x 10^{-6} (K^{-1}) along c-axis, Single layer	CTEx 10^{-6} (K^{-1}) along c-axis, (30/10) nm	CTEx 10^{-6} (K^{-1}) along c-axis, (20/10) nm	CTEx 10^{-6} (K^{-1}) along c-axis, (10/10) nm
300	2.47	10.05	8.05	12.85	15.95
373	2.79	10.25	8.29	13.23	16.11
473	3.23	10.52	8.61	13.75	16.32
573	3.66	10.79	8.94	14.27	16.52
673	4.10	11.06	9.27	14.78	16.73
773	4.53	11.33	9.59	15.30	16.94
873	4.97	11.59	9.92	15.82	17.15
973	5.40	11.86	10.24	16.34	17.36
1073	5.84	12.13	10.57	16.86	17.57
1173	6.27	12.40	10.90	1784	17.78
1273	6.71	12.67	11.22	17.03	17.99
1373	7.15	12.94	11.55	18.42	18.21

Table 2: The CTE of t-ZrO_2 of single and multilayers along c-axis.

4. Conclusions

Thermal expansion behavior of c-Y_2O_3 and t-ZrO_2 of the multilayers of ZrO_2/Y_2O_3 multilayer of (30/10) nm, (20/10) nm, (10/10) and (5/10) nm thickness were

investigated by high temperature x-ray diffraction. Several parameters which operate in the phase stabilization of t-zirconia and the variation in the coefficient of thermal expansion of the t-ZrO_2 and c-Y_2O_3 were examined for the samples subjected to two stage heat treatment in the temperature range 300-1373 K. It is noted that the phase stability of nanostructured multilayers can be different from the stability of the same materials in bulk form because of the increased contribution from surface and interface effects. Some of the important conclusions are the following:

(i)The stabilization of tetragonal zirconia in these multilayers is promoted in the entire temperature range. The phase stabilization in these multilayers is promoted because of higher solubility and structural similarity of zirconia and yttria and thermally generated oxygen vacancies in zirconia.

(ii) The co-efficient of thermal expansion of t-ZrO_2 and c-Y_2O_3 of the multilayers are found to be higher than those of single layers. The co-efficient of thermal expansion of t-ZrO_2 is found to increase with decrease in layer thickness of ZrO_2. The larger ionic size and increased solubility of yttria in zirconia, enhanced concentration of oxygen vacancies in zirconia and increased number of interfaces and interfacial area with decreasing layer thickness of zirconia could contribute to the increased co-efficient of thermal expansion observed in these multilayers.

5. Acknowledgments

References

[1] Shapiro J. M., Taylor D. R., Graham G.M., A Sensitive Dialometer for use at Low Temperatures, Can. J. Phys., 42, 835-847, 1964.

[2] Jacobs S.F., Bradford J.N., Berthold J.W., Ultraprecise measurement of thermal coefficients of expansion, Appl. Opt., 9, 2477-2480, 1970.

[3] James J.D.,Spittle J.A., Brown S.G.R., Evans R.W., A review of measurement techniques for the thermal expansion coefficient of metals and alloys at elevated temperatures, Meas. Sci. Technol., 12, R1-R15, 2001.

[4] Batchelder D.N., Simmons R.O., Lattice constants and thermal expansivities of silicon and of calcium fluoride between 6 and 322 K, J. Chem. Phys., 41, 2324-2329 ,1964.

[5] Rafla-Yuan H., Hichwa B.P., Allen T.H., Noncontact method for measuring coefficient of linear thermal expansion of thin films, J. Vac. Sci. Technol. A;, 16, 3119-3122. 1998.

[6] Fang W., Tsai H. C., Lo C.Y., Determining thermal expansion coefficients of thin films using micromachined cantilevers, Sensors and actuators , 77, 21-27, 1999.

[7] Madan A, Wang Y.Y., Barnett S.A., Engstrom, C., Ljungcrantz H., Hultman L., Grimsditch M., Enhanced mechanical hardness in epitaxial onisostructural Mo/NbN and W/NbN superlattices J. Appl. Phys., 84, 776, 1998.

[8] Madan A., Barnett S.A., Mishra A, Kung H., Nastasi M., Structure, stability, and mechanical properties of epitaxial W/NbN superlattices, J. Vac. Sci. Technol. A., 19, 952, 2001.

[9] Barnett S.A., Madan A., Hardness and stability of metal–nitride nanoscale multilayers. Scr.Mater., 50, 739, 2004.

[10] Balakrishnan G., Kuppusami P., Murugesan, S., Ghosh, C., Divakar, R., Mohandas E., Sastikumar D., Characterization of Al_2O_3/ZrO_2 nano multilayer thin films prepared by pulsed laser deposition,Mater. Chem. Phys., 133, 299-303, 2012.

[11] Balakrishnan G., Kuppusami, P., Murugesan S., Ghosh C., Divakar R., Mohandas E., Sastikumar D., Thermal stability of CeO_2/ZrO_2multilayer thin films prepared by pulsed laser deposition, Trans. IIM, , 64 (3), 297-299, 2011.

[12] Barshilia H.C., Deepthi B., Rajam K.S., Stabilization of tetragonal and cubic phases of ZrO_2 in pulsed sputter deposited ZrO_2/Al_2O_3 and ZrO_2/Y_2O_3 nanolayered thin films J. Appl. Phys.,104,113532 , **2008**.

[13] Mishra M., Kuppusami P., Murugesan S., Ghosh C. , Divakar, R., Singh A., Mohandas E., Thermal stability and therma l expansion behaviour of ZrO2/Y2O3 multilayers deposited by pulsed laser deposition technique, Mater. Chem. Phys.,162, 592-607, **2015**.

[14] Lebrun G., Denault J., Effect of annealing on the thermal expansion and residual stresses of bidirectional thermoplastic composite laminates, Compos. Part A-Appl S., , 41, 101-107, 2010.

[15] Holland T.J.B., Redfern S.A.T., UNITCELL: a nonlinear least-squares program for cell-parameter refinement implementing regression and deletion diagnostics J. Appl. Crystallogr., 30, 84-85, 1997.

[16] James J.D., Spittle J.A., Brown S.G.R., Evans R.W., A review of measurement techniques for the thermal expansion coefficient of metals and alloys at elevated temperatures Meas. Sci. Technol., 12, 3, R1-R15, 2001.

[17] Shin M., Barnett S.A., Effect of superlattice layer elastic moduli on hardness Appl. Phys. Lett., , 64, 61-63, 1994.

[18] Duwez P., Brown F.H., Odell J.F., The Zirconia-Yttria SystemJ. Electrochem.Soc., 98 (9), 356-362,1951.

[19] Shukla S., Seal S., Mechanisms of room temperature metastable tetragonal phase stabilisation in zirconia Int. Mater. Rev., , 50, 45-64, 2005.

[20] 20. Limarga A. M., Sujano W., Hon Y. T., Mechanical properties and oxidation resistance of plasma-sprayed multilayered Al2O3/ZrO2 thermal barrier coatings, Surf. Coat. Technol., 197, 93-102, 2005.

[21] **21**. Kim D., Hyun S., Kim S., Yashima M., Effective Ionic Radius of Y3+ Determined from Lattice Parameters

of Fluorite-Type HfO2 and ZrO2 Solid Solutions, *J. Am. Ceram. Soc.*, , 77, 597-599, 1994.

[22] 22. Karan N.K., Katiyar R.S, Maiti T., Guo, R., Bhalla A.S.*,* Raman spectral studies of Zr4+-rich BaZrxTi1−xO3 (0.5⩽ x⩽ 1.00) phase diagram *J. Raman Spectr.,* **2009**, 40 (4), 370.

[23] 23 Friedel J., LX. Deviations from Vegard's law, Philosophical Magazine Series 7, 46 (7), 514-516, 1955.

[24] 24. Roy R., Agarwal D.K., McKinstry H.A., *Ann. Rev. Mater. Sci.*, , 19, 59-81, **1989**.

[25] 25.   Grover V., Tyagi A.K., Phase relations, lattice thermal expansion in CeO_2–Gd_2O_3system,   and stabilization of cubic gadolinia, Mater. Res. Bull., , 39, 859-866,2004.

[26] 26.   Chanchal Ghosh,; Divakar Ramachandran,; Balakrishnan, G.; Kuppusami,P.; Mohandas, E., HRTEM investigation of phase stability in alumina–zirconia multilayer thin films Bull. Mater. Sci.,38, 401-407, 2015.

[27] 27. Hayashi H., Suzuki M., Inaba H., Thermal expansion of Sr-and Mg-doped LaGaO 3, *Solid State Ionics*, 128, 131-139,2000.

[28] 28.   Hayashi, H.; Kanoh, M.; JiQuan, C.; Inaba, H.; Wang, S.; Dokiya, M.; Tagawa, H., Thermal expansion of Gd-doped ceria and reduced ceria, *Solid State Ionics,* 132, 227-333, 2000.