

Study of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ (5 nm/20nm) Nanolaminate Composite

G. Balakrishnan*, A. Wasy*, Ha Sun Ho*, P. Sudhakara*, S.I. Bae* and J.I. Song*⁺

ABSTRACT

A nanolaminate consisting of alternate layers of aluminium oxide (Al_2O_3) (5 nm) and zirconium oxide (ZrO_2) (20 nm) was deposited at an optimized oxygen partial pressure of 3×10^{-2} mbar by pulsed laser deposition. The nanolaminate film was analysed using high temperature X-ray diffraction (HTXRD) to study phase transition and thermal expansion behaviour. The surface morphology was investigated using field emission scanning electron microscopy (FE-SEM). High temperature X-ray diffraction indicated the crystallization temperature of tetragonal zirconia in the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ multilayer -film was 873 K. The mean linear thermal expansion coefficient of tetragonal ZrO_2 was $4.7 \times 10^{-6} \text{ K}^{-1}$ along a axis, while it was $13.68 \times 10^{-6} \text{ K}^{-1}$ along c axis in the temperature range 873-1373 K. The alumina was in amorphous nature. The FESEM studies showed the formation of uniform crystallites of zirconia with dense surface.

Key Words : Thin films, Ceramic, Composites, Multilayers, Alumina and zirconia, Thermal expansion

1. Introduction

Layered composites, in which ceramic layers of material are combined to create the properties superior to those of the constituent layer materials, have now, emerged as an interesting area of research. These structures provide the advantage of tailoring the properties by stacking layers of different compositions in a suitable sequence. Nanoscale multilayers have tremendous interface area density making interfacial and surface energies predominant, which encourages the stabilization of metastable structures, increase the solubility limits in immiscible systems, favour the development of unusually large strains and enhance tribological properties or wear/corrosion resistance. Interfaces act as a barrier to dislocation motion and/or crack deflection but also reduced crystallite sizes, which are factors for increased yield strength and hardness enhancement found in a larger variety of metallic or nitride based multilayers, when the bilayers period decreases in the 2-5 nm range[1]. It is known that pure zirconia (ZrO_2) has three phases such as monoclinic (m), tetragonal (t) and cubic (c). The monoclinic phase is stable up to 1443 K, the tetragonal phase is stable in the temperature

range 1443-2643 K and the cubic phase in the temperature range 2643-2953 K[2]. For most engineering applications, which require high operation temperature, zirconia is stabilized in its tetragonal structure. The transformation of the high temperature phase to stable monoclinic phase is accompanied by a volume change of $\sim 3\text{-}5\%$ [3,4]. This volume increase may cause high residual stresses and even lead to delamination of ZrO_2 films from the substrate. Therefore, it is important to stabilize the high temperature phases (tetragonal and cubic) at room temperature for many applications. The aim of the present work is to stabilize the high temperature phase (tetragonal or cubic) of zirconia at a temperature as low as possible.

Different mechanisms can be employed to retain the tetragonal phase of zirconia at room temperature: (i) doping metallic oxides, such as yttria (Y_2O_3), alumina (Al_2O_3), magnesia (MgO) and some rare earth oxides, or (ii) controlling the crystallite size of the high temperature phase (tetragonal) within a few nm[5,6]. $\text{Al}_2\text{O}_3/\text{ZrO}_2$ multilayer approach is an important method to stabilize the high temperature tetragonal phase[7-9]. The multilayer geometry is also effective for the improvement of the thermal shock life of thermal barrier coatings (TBCs), because no

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* Department of Mechanical Engineering, Changwon National University

*+ Department of Mechanical Engineering, Changwon National University, Corresponding author(E-mail:jjisong@changwon.ac.kr)

single material satisfies the requirements of TBCs[10]. Besides this application, Al₂O₃/ZrO₂ multilayers are widely used in several technological applications such as antireflection coating on micro optics, dielectric material in metal oxide semiconductor (MOS) devices and high transparent materials in optical applications[10-12]. In the present work, an attempt has been made to prepare a Al₂O₃/ZrO₂ film and hence to stabilize the tetragonal phase at a temperature as low as possible using pulsed laser deposition (PLD). PLD is a flexible, simple and controllable method for making high quality thin films of metallic oxides. One of the major advantages is that the stoichiometry can be retained in the deposited films. The rapid rate of ablation from a few nm thickness of the target surface promotes the constituents of the target to evaporate congruently and to retain stoichiometry in the film formation[13].

2. Experimental Details

Al₂O₃ (99.99% purity) and ZrO₂ (99.99%) pellets of 25 mm diameter and 3 mm thickness were prepared and sintered at 1673 K for 6 hours and used as targets for PLD. The deposition was performed using a KrF excimer laser and other deposition parameters are given in Table 1.

Table 1 Deposition parameters of multilayer film

Laser	KrF (248nm)
Energy density	3 J/cm ²
Repetition rate	10 Hz
Target-substrate distance	4.5 cm
Substrate	Si (100)
Substrate temperature	300 K
Oxygen partial pressure	3.0×10 ⁻² mbar
Pulse duration	30 ns
Target	α-Al ₂ O ₃ & ZrO ₂
Base vacuum	2.0×10 ⁻⁵ mbar
Alumina layer thickness	5 nm
Zirconia layer thickness	20 nm

Si (100) oriented substrates (N-type phosphorous doped with a resistivity of 20-30 Ω-cm) were used for the thin film deposition. No special preparation was carried out to remove the native oxide present on the Si substrates. Prior to the deposition of Al₂O₃/ZrO₂ multilayer thin films, the chamber was evacuated to 2×10⁻⁵ mbar using a turbo molecular pump backed with a rotary pump. The target was rotated and translated with an electric motor to avoid pitting on the target. Multilayer, which consists of a Al₂O₃ layer of 5 nm thickness and a ZrO₂ layer of 20 nm were deposited at an optimized oxygen partial

pressure of 3×10⁻² mbar at room temperature. A total of 40 bilayers were deposited. Before the deposition of the multilayers, deposition rates of the individual layers were determined accurately by measuring the thickness of each layer using a Dektak profilometer (DEKTAK 6M-stylus profiler). The multilayer sample consists of alternate layer of Al₂O₃ and ZrO₂ with a total thickness of 1.0 μm was in-situ heat-treated upto 1373 K in X-ray diffractometer attached with a curved position sensitive detector and a Buhler 2.4 HDK high temperature camera to study the microstructural and thermal properties. A heating rate of 10 K/min, cooling rate of 25 K/min and soaking time of 5 minutes were used. The patterns were recorded from 300 to 1373 K in steps of 100 K in a vacuum of the order of ~ 2×10⁻⁵ mbar. All patterns were recorded for 30 minutes. The surface morphology of the film was analysed using a field emission scanning electron microscope (TESCAN, Model: MIRA II LMH) equipped with a high brightness schottky emitter.

3. Results and discussion

Figure 1 shows the HTXRD pattern of a Al₂O₃/ZrO₂ (5/20 nm) multilayer film with 40 bilayers in the temperature range 300 -1373 K. The broadening of the peak at an angle of 32° occurred due to the overlapping of peaks of monoclinic and tetragonal phases. The films were amorphous at low temperatures. At 873 K, the film showed crystalline nature of zirconia. The peaks (101), (002), (110) (102), (200), (103), (211), (004), (220), (222) and (301) corresponding to the tetragonal phase, and a weak peak of (-111), corresponding to monoclinic zirconia, were observed [14]. As the temperature increased from 873 K to 1373 K, the intensity of the (101) peak increased compared to the intensity of the (-111) of the monoclinic phase, indicating an increase of the tetragonal phase content with increasing annealing temperature. It was interesting to note that the alumina remains in amorphous state throughout the range of annealing temperature. It is believed that when the alumina films are formed with thickness less than the critical thickness, the temperature of crystallization also increases significantly and therefore the films are amorphous when the thickness is about 5 nm[15,16].

It is seen from the Fig.1 that the phase content of tetragonal phase is significantly higher than that of the monoclinic phase and their fractions change slightly at higher annealing temperatures. There was no complete transformation of monoclinic phase into tetragonal phase or vice-versa in the above temperature range (300-1373 K).

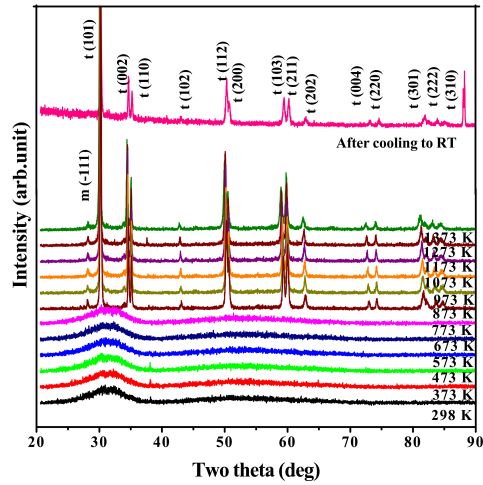


Fig. 1 HTXRD pattern of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ (5 nm/20 nm) film deposited at 300 K.

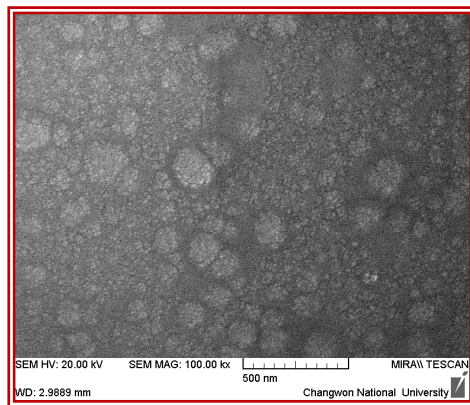


Fig. 2 FESEM image shows the surface morphology of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ (5/20 nm) film deposited on Si (100) at 300 K.

The phase composition (monoclinic and tetragonal) was calculated as a function of temperature. The weight fraction of the monoclinic and tetragonal phases of zirconia is given by equation (1)[17]:

$$V_m = \frac{I_m(\bar{1}11)}{\{I_m(\bar{1}11) + I_t(101)\}} \quad (1)$$

$$V_t = 1 - V_m$$

where I_m is the peak intensity of monoclinic and I_t is the peak intensity of tetragonal phases. The weight fraction of the monoclinic and tetragonal phases were determined qualitatively using the reflections ($\bar{1}11$) of monoclinic and (101) tetragonal phases [18].

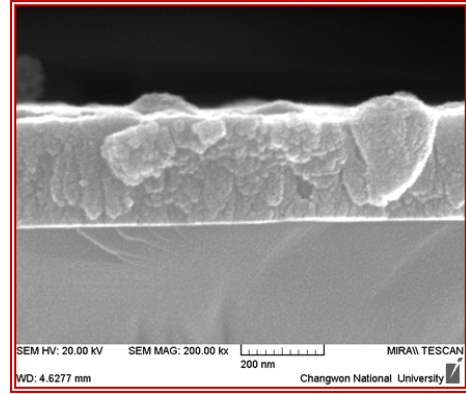


Fig. 3 FESEM shows the cross sectional view of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ (5/20 nm) film deposited on Si (100) at 300 K.

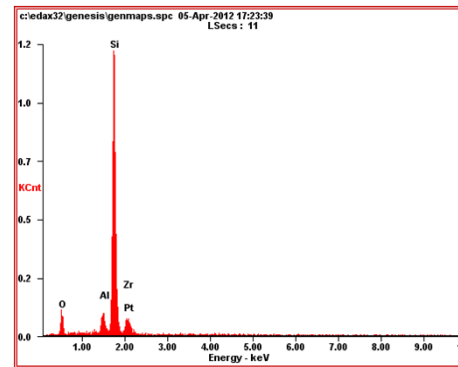


Fig. 4 EDAX shows the presence of Al_2O_3 and ZrO_2 in the film.

Table 2 Lattice parameters and thermal expansion coefficients of the t- ZrO_2 of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ (5 nm/20 nm) multilayer film annealed at high temperature.

Temp (K)	a (Å)	c (Å)	Unit cell volume (Å ³)	$\alpha_a \times 10^{-6}$ (K ⁻¹)	$\alpha_c \times 10^{-6}$ (K ⁻¹)	$\alpha_v \times 10^{-6}$ (K ⁻¹)
873	3.651	5.169	68.913	----	----	----
973	3.653	5.177	69.093	5.477	15.476	26.11
1073	3.654	5.183	69.185	4.11	13.542	19.73
1173	3.655	5.189	69.341	3.65	12.897	20.71
1273	3.658	5.195	69.530	4.80	12.575	22.39
1373	3.661	5.205	69.762	5.48	13.932	24.64

The tetragonal phase content was in the range of 81-97% and the monoclinic phase content was 3-19% for 5/20 nm multilayer film. The lattice parameters were calculated for t- ZrO_2 in 5/20 nm multilayer film. The lattice parameter a , increased from 3.651 Å to 3.661 Å, while the parameter c , increased from 5.170 Å to 5.205 Å as the temperature increased from 873 K to 1373 K. The lattice parameters, a

and c with respect to temperature are given in Table 2. The percent linear thermal expansion $\{(\Delta a/a) \times 100\}$ along the a and c $\{(\Delta c/c) \times 100\}$ axes and percent lattice (volume) thermal expansion were calculated as a function of temperature using the lattice parameters a and c . The mean linear thermal expansion coefficients were calculated along the a and c axes using equation (2) [19]:

$$\begin{aligned}\alpha_a &= \frac{1}{a_{CT}} \left[\frac{a_T - a_{CT}}{T - CT} \right] \\ \alpha_c &= \frac{1}{c_{CT}} \left[\frac{c_T - c_{CT}}{T - CT} \right] \\ \alpha_v &= \frac{1}{v_{CT}} \left[\frac{v_T - v_{CT}}{T - CT} \right]\end{aligned}\quad (2)$$

where a_{CT} , c_{CT} and v_{CT} are the lattice constants at crystallization temperature along the a , c axes and unit cell volume, respectively, a_T , c_T and v_T are the lattice constants along a , c directions and unit cell volume respectively at temperature T , α_a is the thermal expansion coefficient of cell parameter a , α_c is the thermal expansion coefficient of cell parameter c , α_v is the volume thermal expansion coefficient and CT is the crystallization temperature at which crystallization of the ZrO₂ is observed.

The percent thermal expansion along the a and c axes were calculated as a function of temperature for 5/20 nm film of Al₂O₃/ZrO₂. It showed a maximum thermal expansion value of 0.3 % along the a axis and 0.7 % along the c axis at a temperature of 1373 K. The maximum percent lattice thermal expansion was 1.2 % at 1373 K. Table 2 gives a , c values, unit cell volume, and thermal expansion coefficients with respect to temperature. The mean linear thermal expansion coefficient was $4.7 \times 10^{-6} \text{ K}^{-1}$ along the a axis, while it was $13.68 \times 10^{-6} \text{ K}^{-1}$ along the c axis in the temperature range 873-1373 K. The thermal expansion coefficient along the c axis is around 3 times that of the a axis.

Figure 2 shows the surface morphology of the Al₂O₃/ZrO₂ nanolayers deposited on Si (100) substrate. It shows the dense and uniform formation of the crystallites. Figure 3 shows the cross sectional view of the nanolaminate and formation of island growth of the film. Teixeira et al.[20], deposited ZrO₂/Al₂O₃ nanolayers films by DC reactive magnetron sputtering with O₂ and Ar gas mixture, at constant temperature, bias and work pressure. They reported that the high temperature tetragonal phase content increased as the nanolayers get thinner. Multilayers[6] prepared by DC magnetron sputtering with ZrO₂ layer thicknesses

between 8-20 nm showed excellent thermal stability after annealing and the Raman peak position shifts to lower wave numbers with an increase of compressive stress. ZrO₂ was combined with other metal oxides in multilayer nanolaminate films such as ZrO₂-Al₂O₃, ZrO₂-Y₂O₃, and ZrO₂-TiO₂[21]. The films were grown by sequential sputter deposition of individual oxide layers from metal targets using radio-frequency-excitation with O₂-bearing discharges. As the thickness of individual layers decreased, interfaces were found to play an increasingly important role in determining the nanolaminate's overall properties. These nanolaminates had different thermodynamic driving forces for interfacial cation mixing. It is found that thermodynamic considerations strongly influence both phase formation within layers and at interfaces, where deposition are carried out at far from equilibrium[22]. Pseudo binary phase diagrams could be used to predict interfacial cation mixing in the nanolaminates. However, size effects must be considered to predict specific structures. In the absence of pseudo epitaxy, size effects play a significant role in determining the nanocrystalline phases that form within a layer (e.g. t-ZrO₂, tetragonal HfO₂, and orthorhombic HfO₂) and at interfaces (e.g. monoclinic (Zr, Ti)O₂). Their formation is understood in terms of self-assembly into the lowest energy structure in individual critical nuclei. Barshilia et al. [23] prepared nanolayer thin films of ZrO₂/Al₂O₃ using pulsed sputtering to study the stabilization of various polymorphs of ZrO₂. These films were deposited at various substrate temperatures (623-973 K), varying individual layer thicknesses (1.9-25.2 nm) and modulation wavelengths (bilayer thickness) ($\Lambda=9.6-32.7\text{nm}$). X-ray diffraction data showed monoclinic and amorphous structures for ZrO₂ and Al₂O₃ thin films, respectively. The tetragonal phase of ZrO₂ (t-ZrO₂) was stabilized for ZrO₂/Al₂O₃ nanolayer thin films prepared with bilayers thickness (Al₂O₃ layer thickness + ZrO₂ layer thickness) of ≤ 13.8 nm. They demonstrated that a critical ZrO₂ thickness (≤ 10.5 nm at a substrate temperature of 973 K) was required in order to stabilize the t-ZrO₂ phase, which was in agreement with thermodynamically derived critical radius for the stabilization of the tetragonal phase.

Pure zirconia films and zirconia-alumina nanolaminate films grown by reactive sputter deposition were studied by high resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) [24]. The results showed that there was a significant difference between the transformation behaviour of dopant-stabilized and that of undoped nanocrystals of tetragonal zirconia. In the former, the metastable tetragonal phase was shown to transform to the monoclinic phase under application of stress. In contrast, no such transformation was

observed under similar stress conditions in tetragonal zirconia nanocrystallites, when the alumina layers were preserved. Therefore, the tetragonal zirconia nanocrystallites in zirconia-alumina nanolaminates are less likely to undergo transformation than the dopant-stabilized zirconia microcrystallites in zirconia-alumina composites. Alumina influences the growth of the zirconia layer and provides a template for the stabilization of metastable phase of zirconia. The monoclinic to tetragonal phase transformation depends on physical and chemical factors and the layer thickness is the most important influencing parameter on stabilization of tetragonal zirconia. The critical thickness of the metastable phase depends on a combination of bulk free energy, interfacial energy, and surface energy[19]. When the layers are very thin, the interfacial and surface energies dominate both the bulk and the strain energy terms, which could promote the formation of a metastable phase with a low interfacial energy. If the layers have thickness above a critical thickness, the interfacial energy term becomes less important and bulk formation energies dominate. This kind of multilayer is not only interesting in terms of applications but also provides better understanding in the materials properties when subjected to high temperatures. In the present research work, ZrO₂ layer thickness is 20 nm and the Al₂O₃ layer thickness is 5 nm, so that the very thin layer of Al₂O₃ (5 nm) is not able to provide the enough compress stress on thicker ZrO₂ layer of 20 nm. Hence, the Al₂O₃ layer (5 nm) is not able to provide the enough local compressive stress to suppress the monoclinic phase. Therefore the tetragonal crystallization occurred only at 873 K. Therefore it is necessary to reduce the ZrO₂ layer thickness to less than 20 nm, so that it could be possible to attain the tetragonal phase at lower temperature.

4. Conclusion

A nanolaminate structure consisting of alternate layers of Al₂O₃ and ZrO₂ were fabricated using pulsed laser deposition. High temperature X-ray diffraction indicated a crystallization temperature of tetragonal zirconia in the Al₂O₃/ZrO₂ multilayers at 873 K. The mean linear thermal expansion coefficient of tetragonal zirconia was $4.7 \times 10^{-6} \text{ K}^{-1}$ along *a* axis, while it was $13.68 \times 10^{-6} \text{ K}^{-1}$ along *c* axis in the temperature range 873-1373 K. The FESEM studies showed a uniform distribution of crystallites and dense surface of the film.

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