E-Beam Deposition of Scandia-Stabilized Zirconia (ScSZ) Thin Films Co-Doped with Al

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Abstract: Scandia alumina stabilized zirconia (ScAlSZ) thin films were deposited using e-beam evaporation, and the effects of deposition parameters on the structure and chemical composition were investigated. The analysis of thin films was carried out using Energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), X-Ray Diffraction Analysis (XRD) and Raman spectroscopy methods. It was found that the chemical composition of ScAlSZ thin films was different from the chemical composition of the initial powder. Moreover, the Al concentration in thin films depends on the deposition rate, resulting in a lower concentration using a higher deposition rate. XPS analysis revealed that ZrOx, oxygen vacancies, high concentrations of Al2O3 and metallic Al exist in thin films and influence their structural properties. The crystallinity is higher when the concentration of Al is lower (higher deposition rate) and at higher substrate temperatures. Further, the amount of cubic phase is higher and the amount of tetragonal phase lower when using a higher deposition rate.

Keywords: co-doped zirconia; e-beam physical vapor deposition; thin films; ceramics; Raman spectroscopy; X-ray diffraction

1. Introduction

In the last few decades, materials based on zirconium oxide (ZrO2) have been studied intensively due to their unique combination of thermal stability, strength, good electrochemical characteristics and low cost [1]. Pure zirconia exhibits three polymorphic types: Monoclinic, tetragonal and cubic. The monoclinic phase is retained up to around 1170 °C. The structural changes to a tetragonal phase occur above this temperature. At a temperature of 2370 °C, the tetragonal phase transforms into a cubic fluorite structure, and melts at 2680 ± 50 °C [2,3]. During the transformation from the monoclinic to the tetragonal phase, there is a volume change of around 4%, which can induce defects in the material [4]. The mechanism for ionic conductivity is based on the oxygen vacancies formation, requiring high energy to remove oxygen atoms from the crystal lattice; therefore, pure zirconia is mainly an insulator. Zr4+ can be replaced by divalent or trivalent cations creating oxygen vacancies, and exhibits higher ionic conductivity [3]. Moreover, dopants can stabilize the cubic structure at room temperature. The most investigated are Y2O3, Yb2O3, Sc2O3, Gd2O3, Dy2O3, Nd2O3, Sm2O3, CaO, and MgO, etc. [4]. The stability of ceramic materials depends on the type and concentration of the dopant. Sc2O3 is considered as one of the most promising dopants. Scandia stabilized zirconia (ScSZ) is an interesting ceramic material that can be widely used in many applications, such as electrochemical oxygen
gas sensors, oxygen pumps, catalytic support medium, etc. [1]. ScSZ has a unipolar conductivity, provided only by the oxygen ions in a wide range of temperatures and pressures [5,6]. The oxygen vacancy-induced ionic conductivity of zirconia-based ceramics is predominant up to sufficiently high temperatures (1200 °C) [2]. Consequently, ScSZ could compete with yttria-stabilized zirconia (YSZ) at intermediate temperatures (600 °C), where it has higher ionic conductivity than YSZ [7]. Sometimes, small concentrations (1–2 mol %) of additional dopants (co-doping) are used to increase the concentration of scandia in ZrO2, maintaining cubic structure at the same time. Rare-earth elements or their oxides, such as CeO2, Gd2O3, Sm2O3, Bi2O3, Yb2O3, and Al2O3 [8–10], are good candidates to be co-dopants for ScSZ structures. For example, co-doping by Al2O3 can lead to a change in the structure, influencing mechanical and electrical properties [11–16]. However, the desired effect is obtained using only low concentrations of Al2O3 (<1 wt.%). The great majority of investigations are concentrated on the material pellets and powders. Al co-doped ScSZ thin films and their properties based on the phase transitions have not been studied enough. The properties of thin films are strongly related to the formation method and formation parameters. The e-beam physical vapor deposition method is one of the most suitable methods for forming ceramic layers. A high temperature is produced by the collision of the electrons and the material in the crucible. It can increase by over 3000 °C. The melting temperature for most of the metal oxides is lower. The deposition rate can be adjusted over a wide range using the e-beam evaporation technique, which is not possible to do using the magnetron sputtering technique for metal oxides. Thin films are dense and homogeneous. Moreover, the structure of thin films does not depend on the structure of the initial material because zirconia-based materials evaporate by partial dissociation. However, there are some disadvantages to this method. One of them is that materials with different melting temperatures evaporate at different rates. So, it is hard to deposit thin films with the desired composition if the material is multicomponent. Scandia and alumina stabilized zirconia (ScAlSZ) are not exceptions. Therefore, in our work, (Sc2O3)0.06(Al2O3)0.01(ZrO2)0.93 (6ScAlSZ) thin films were deposited using an e-beam physical deposition system by changing the deposition rate (0.2–1.6 nm/s) and temperature (300 and 600 °C). After that, the chemical composition and structural properties were investigated. EDS and XPS were used for the determination of chemical composition. The structure analysis of zirconia materials is complicated due to its polymorphism. The peaks in the XRD patterns of crystalline phases (e.g., tetragonal and cubic) have similar positions and can overlap [17]. Therefore, XRD analysis was supplemented by Raman spectroscopy measurements. Raman spectroscopy is a very sensitive method and can give information about crystal structure, chemical composition and oxygen vacancies [13,14]. Moreover, there is plenty of literature describing different phases of ZrO2, which is helpful for detailed analysis of the structure: Monoclinic (m) [18–20], tetragonal (t) [2,17–20], rhombohedral (β) [2,18] and cubic (c) [2,7,16,18].

2. Materials and Methods

Scandia alumina stabilized zirconia (Sc2O3)0.06(Al2O3)0.01(ZrO2)0.93 (6ScAlSZ) micro powders (Nexceris, LLC, Fuelcellmaterials, Lewis Center, OH, USA) were used as evaporation materials. The particle size (D90) was 0.5–0.7 μm and the specific surface area of the powders was 8–10 m2·g−1. Thin films (1.5 μm) of ScAlSZ were deposited by the e-beam physical vapor deposition system “Kurt J. Lesker EB-PVD 75” (Kurt J. Lesker Company, Pittsburg, PA, USA) on preheated Alloy 600 (Fe–Ni–Cr) substrates. The deposition rate was in the range of 0.2–1.6 nm/s and the substrate temperatures were 300 and 600 °C. The pressure during the deposition process was 9 × 10−3 Pa. The crystal structure of formed ceramic thin films was determined by X-ray diffraction (XRD, Bruker, Billerica, MA, USA) “Bruker D8 Discover” at 2θ angle in a 20°–70° range using Cu Kα (λ = 0.154059 nm) radiation, 0.01° steps and a Lynx eye PSD detector. The calculations of the crystallite size were done using the “TOPA4.1” software. The identification of diffraction peaks was performed using the EVA Search-Match software and PDF-2 database. The thicknesses of formed thin films were estimated using a profilometer (Ambios Technology XP-200, Keep Looking Ahead (KLA), San Jose, CA, USA). Raman spectroscopy measurements were carried out by inVia (Renishaw, Gloucestershire, UK) at room
temperature. The 532 nm wavelength diode laser and 4 μm diameter of the laser were used during the measurements. The laser spot was focused on a sample using a 50× objective (NA = 0.75, Leica, Wetzlar, Germany). The integration time of signals was 15–30 s, which were accumulated 5 times and averaged. The diffraction gratings (2400 grooves/mm) provided spectral resolution of 1 cm⁻¹. A Peltier cooled charge-coupled device (CCD) camera detector was used to record the data (Renishaw, Gloucestershire, UK) (1024 × 256 pixels). The phase content of cubic, tetragonal and monoclinic phases in the ScAlSZ thin films were calculated using the relation between the most characteristic peaks of the Raman spectra [21]. Further, the factor $k$ [22,23] was used during the calculation of the phase ratio, where $k$ is the factor converting intensities between XRD and Raman spectra of the reference materials. The positions of Raman peaks were determined by fitting the data to the Lorentz line shape using a peak fit option in the OriginPro 2016 software. The phase ratio calculations were done according to the formula [21–23]:

$$\delta_c = \frac{I_c}{k(I_m + I_t) + I_c}$$

where $I_{c,m,t}$—peak intensities of cubic, monoclinic and tetragonal phases in Raman spectra, $k = 0.97$.

The energy-dispersive X-ray spectroscopy “BrukerXFlash QUAD 5040” (EDS, Bruker, Billerica, MA, USA) was used to examine the elemental composition of formed ceramic thin films. Chemical analysis was estimated by the means of an X-ray photoelectron spectrometer (XPS, PHI Versaprobe 5000, ULVAC-PHI, Chigasaki, Kanagawa, Japan). The parameters were Al Kα (1486.6 eV) radiation, 25 W power, 100 μm beam size, 45° measurement angle, 187.580 eV pass energy, 1 eV resolution for Survey Spectrum, and 0.1 eV for detailed chemical analysis.

3. Results

X-ray diffraction patterns show that 6ScAlSZ powder has the following mixture of phases: Monoclinic (JCPDS No. 04-014-8566) and cubic (JCPDS No. 01-089-5485) of ScSZ, and rhombohedral (JCPDS No. 04-015-8608) of Al₂O₃ (Figure 1a). The monoclinic and cubic phases are predominant and show sharp peaks at (111), (200), (122), and (222), and some minor peaks at (011), (012), (002), (110), (211), (113), (024), (202), (116), and (300). The Raman spectra of 6ScAlSZ powder give similar information as XRD (Figure 1b). A comparison of the Raman spectra of initial powder and the literature data is in Figure 1b. Raman peaks were detected at 147, 178, 190, 221, 261, 332, 381, 473, 536, 559, 620, and 635 cm⁻¹, and around 750–1000 cm⁻¹ positions. They belong to the monoclinic (m-ZrO₂), cubic (c-ZrO₂), rhombohedral (β-Al₂O₃) and tetragonal (t-ZrO₂) phases of 6AlScSZ powders. The former one was not found by doing XRD analysis. The Raman bands at 178, 190, 221, 332, 473, and 559 were allocated to the Raman-active modes for the monoclinic phase of ZrO₂ (m-ZrO₂), $A_g$ at 178–190 cm⁻¹, $B_{1g}$ at 221 cm⁻¹, $B_{1g}$ at 332 cm⁻¹, $B_{2g}$ at 381 cm⁻¹, $A_{g}$ at 473 cm⁻¹ and $A_{g}$ at 559 cm⁻¹ [18–20,24,25]. The bands at 147, 261, and 635 cm⁻¹ were assigned to the Raman-active modes for the tetragonal phase of ZrO₂ (t-ZrO₂), $B_{1g}$ at 147 cm⁻¹, $E_{g}$ at 261 cm⁻¹ and $A_{1g}$ at 635 cm⁻¹ [10,20,26–28]. The cubic zirconia (c-ZrO₂) fluorite structure with the Fm3m space group and F$_{2g}$ Raman mode symmetry should be centered between 605 and 630 cm⁻¹, and the peak for Al₂O₃ is centered at 418 cm⁻¹ [2,10,18,19,23,27]. The peaks at 261 cm⁻¹ were assigned only for t-ZrO₂, and the peak at 178 cm⁻¹ only for m-ZrO₂. The band at 473 cm⁻¹ was stronger than the band at 635 cm⁻¹ for the monoclinic phase, and the reverse is true for the tetragonal phase. The above-mentioned are the two main differences in the Raman spectra between the monoclinic phase and the tetragonal phase of zirconia. Furthermore, the bands between 473 and 635 cm⁻¹, which are characteristic for the monoclinic phase, are not visible for the tetragonal phase [29]. Therefore, it is possible to conclude that the Raman spectra of the investigated initial powder of 6ScAlSZ show characteristic peaks of monoclinic (m-ZrO₂), tetragonal (t-ZrO₂) and cubic (c-ZrO₂) zirconia.

The elemental composition of deposited ScAlSZ thin films fluctuates when using different deposition parameters according to the EDS measurements (Table 1). The mean concentrations of O₂, Al, Sc and Zr are 52.0 ± 1.5, 10.2 ± 4.2, 5.4 ± 1.8, and 32.6 ± 2.5 at.% respectively. Correlation between the
deposition parameters and the concentrations of O$_2$, Sc, and Zr was not observed. The concentrations are scattered in the mentioned intervals.

Figure 1. 6ScAlSZ powders: (a) X-ray diffraction (XRD) patterns and (b) Raman shifts.

Table 1. EDS analysis results of ScAlSZ thin films, ($v_d$—deposition rate, $T_d$—substrate temperature during deposition, and $c$—atomic concentration).

| $v_d$, nm/s | $T_d = 300 \, ^\circ$C | $T_d = 600 \, ^\circ$C |
|------------|------------------------|------------------------|
|            | $c_{O_2}$, at.% | $c_{Al}$, at.% | $c_{Sc}$, at.% | $c_{Zr}$, at.% | $c_{O_2}$, at.% | $c_{Al}$, at.% | $c_{Sc}$, at.% | $c_{Zr}$, at.% |
| 0.2        | 51.4                     | 20.2                     | 3.1                     | 25.3                     | 54.2                     | 12.2                     | 3.6                     | 30.0                     |
| 0.4        | 49.5                     | 12.4                     | 3.6                     | 34.5                     | 49.8                     | 12.5                     | 3.4                     | 34.3                     |
| 0.8        | 53.4                     | 3.8                     | 7.4                     | 35.4                     | 50.6                     | 15.8                     | 3.6                     | 30.0                     |
| 1.2        | 51.5                     | 6.4                     | 8.7                     | 33.5                     | 53.6                     | 8.0                     | 6.7                     | 31.8                     |
| 1.6        | 54.1                     | 3.0                     | 6.8                     | 36.0                     | 51.2                     | 7.1                     | 7.1                     | 34.5                     |
| Powder     | 52.0                     | 12.6                     | 3.9                     | 32.5                     | -                       |                          |                          |                          |

However, a relationship between Al and deposition rate was observed. The Al concentration changes non homogeneously with the increase in deposition rate and the substrate temperature (Figure 2). It changes from 20.2 to 3.0 at.% for thin films deposited on 300 °C substrates (Figure 2a), and from 12.4 to 7.1 at.% for thin films deposited on 600 °C substrates (Figure 2b). Furthermore, the mean value of Al concentration is slightly higher for thin films deposited at 600 °C ($c_{Al600} = 9.2$ at.% and $c_{Al600} = 11.1$ at.%). With an increase in deposition rate, the temperature in the crucible increases, influencing the changes in the evaporation rate and vapor concentrations of different elements’ atoms and atoms clusters. A decrease in Al concentration appears due to the different melting temperatures of Al$_2$O$_3$ (2072 °C), Sc$_2$O$_3$ (2485 °C) and ZrO$_2$ (2715 °C). Al$_2$O$_3$ evaporates faster than Sc$_2$O$_3$ and ZrO$_2$. Moreover, the process of thin-film (~1500 nm) formation takes longer at low deposition rates in comparison to higher deposition rates. So, a smaller amount of Al evaporates using a higher deposition rate for the same thickness of thin film.

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The metallic Al or its compound phases in ScAlSZ thin films could form due to high Al concentration that exceed the solubility limit (~7 at.% [30]). Therefore, the chemical composition of ScAlSZ thin films was investigated additionally using the XPS method. The surface of ScAlSZ consists of Sc, Zr, Al, and C compounds, and OH groups (Figure 3a). Detailed information on those compounds was obtained after analysis of the O 1s, Zr 3d, Al 2p and Sc 2p regions (Figure 3b–e). The peak positions were compared with the literature, and it was found that ZrO$_2$ suboxide (3$d_{3/2} = 181.96$ eV, 3$d_{5/2} = 184.36$ eV and O 1s = 530.05 eV), oxygen vacancies (O 1s = 531.40 eV), Sc$_2$O$_3$ (2$p_{3/2} = 401.85$ eV, 2$p_{1/2} = 406.40$ eV and O 1s = 529.65 eV), Al$_2$O$_3$ (2$p_{1/2} = 73.69$ eV and O 1s = 530.85 eV), metallic Al (2$p = 72.90$ eV), AlO(OH) (2$p = 74.82$ eV), OH (O 1s = 532.70 eV), C–O (O 1s = 533.17 eV) and C=O (O 1s = 532.03 eV) exist on the
surface of ScAlSZ thin films [31–35]. Similar positions of binding energies were found for ScSZ by Xue et al. in [28]. OH and CO groups were formed naturally in an ambient environment, and do not influence bulk properties. Therefore, they will be excluded from further discussion. The existence of ZrO\(_2\) and oxygen vacancies, high concentrations of Al\(_2\)O\(_3\) and metallic Al can affect the structural properties of ScAlSZ thin films [36,37].

The XRD measurement proves the previous assumption (Figure 4). ScAlSZ thin films deposited on 300 °C substrates are amorphous at lower deposition rates (0.2–0.4 nm/s) and polycrystalline (17.5–19.7 nm) at higher deposition rates (0.8–1.6 nm/s). According to the search–match procedure, the XRD patterns of thin films have peaks indicating the cubic phase of scandia stabilized zirconia (JCPDS No. 01-089-5485), the tetragonal phase of aluminum stabilized zirconia (JCPDS No. 00-053-0549) and the tetragonal phase of zirconia (JCPDS No. 01-084-9828). We did not observe peaks that could
belong to Al₂O₃. However, it is hard to tell which phase and compound certainly are in the ScAlSZ thin films due to the low number of overlapped and shifted peaks. XRD analysis revealed that the crystallinity is higher using a higher deposition rate, i.e., the peak intensity is higher and the crystallites are larger using a higher deposition rate. The crystallite size is 11.3–18.9 nm using a 0.2–1.6 nm/s deposition rate, respectively. The crystallinity of thin films correlates with the concentration of Al and substrate temperature. It increases with decreasing Al concentration and increasing substrate temperature. The amorphous phases of Al or Al₂O₃ possibly formed in the grain boundaries of ScAlSZ crystallites, and act as impurities. Therefore, grain growth was suppressed at high Al concentrations. The crystallinity decreases by increasing the Al concentration in ZrO₂ thin films deposited using an atomic layer deposition technique [38]. Moreover, it was found that amorphous thin films grow then the concentration of Al is 9.7% [39]. On the other hand, Ishii. T. states that an increasing Al₂O₃ concentration may result from the destruction of the oxygen vacancy ordering of the low temperature rhombohedral phase. A cubic phase was obtained when the Al concentration was 0.5% [9]. Furthermore, the grain size and phase could be influenced by the variations in oxygen content in the formed thin films [40].

![Figure 4. XRD patterns (measured at room temperature) of 6ScAlSZ thin films deposited on Alloy 600 substrates using (a) 300 °C and (b) 600 °C substrate temperatures and different deposition rates from 0.2 to 1.6 nm/s.](image)

To fully identify the structure of the ScAlSZ thin films, Raman measurements were made. The Raman spectra of ScAlSZ thin films have many overlapping peaks, indicating polymorphism. After careful analysis, it was determined that the peaks belong to monoclinic (m-ZrO₂), tetragonal (t-ZrO₂), rhombohedral (Rh-ZrO₂) and cubic (c-ZrO₂) phases (Figure 5). Raman spectra peaks are detected around 150, 200, 264, 460, 627, and 638 cm⁻¹, and peaks between 770 and 900 cm⁻¹ could be attributed to the Raman active lattice phonons and can be assigned to monoclinic and tetragonal phases [24,25]. The Raman shift in the peak position can be explained by the presence of structural heterogeneity in the material. Peak positions greater than 800 cm⁻¹ belong to the second-order active Raman modes [41]. The broad peaks expressed between 149 and 277 cm⁻¹ consist of several peaks, indicating different ZrO₂ phases. Peaks around 198 A₁g match the peaks of the monoclinic ZrO₂ phase [18–20]. The characteristic bands for the tetragonal ZrO₂ phase are expressed by six Raman active modes (A₁g + 2B₁g + 3E_g). Raman peaks detected from 149 to 153 cm⁻¹ and around 638 cm⁻¹ match the A₁g mode of t-ZrO₂ [10,20,26–28]. In Figure 5, the broad peaks expressed between 626 and 630 cm⁻¹ match the peaks of the monoclinic ZrO₂ phase.
since cubic symmetry must be expressed by a broad band around 620–630 cm\(^{-1}\), which is not observed in the Raman spectra of those thin films. Peaks around 687 cm\(^{-1}\) can be interpreted as anomalous luminescence bands.

Moreover, there can be several reasons for wavenumber shifting, including the change of atomic distances or lattice contraction or expansion, for example. So, AlScSZ thin films are polymorphic and consist of monoclinic (\(m\)-ZrO\(_2\)), tetragonal (\(t\)-ZrO\(_2\)), rhombohedral (\(\beta\)-ZrO\(_2\)) and cubic (c-ZrO\(_2\)) phases. The Raman spectra of the ScAlSZ thin films deposited at 0.2 nm/s and 0.4 nm/s at 300 °C, and 0.2, 0.4, and 0.8 nm/s at 600 °C, prove the existence of the cubic phase since cubic symmetry must be expressed by a broad band around 620–630 cm\(^{-1}\), which is not observed in the Raman spectra of those thin films. Peaks around 687 cm\(^{-1}\) can be interpreted as anomalous luminescence bands.

The additional modes that should not appear for the cubic fluorite structure could be explained by the consistent violation of the selection rules, which directly depend on oxygen vacancies that can be reached by the substitution of Zr\(^{4+}\) by Sc\(^{3+}\) [42,43].

The ratios of the cubic phase to the monoclinic, tetragonal phases are from 53% to 59% for 6ScAlSZ, and are generally around 55% (Table 2). By increasing the depositing rate, the amount of cubic phase increases. The obtained results demonstrate that at the 0.2 and 0.4 nm/s deposition rates, the cubic phase is not detected. However, the presence of the broad bands, which are presented in Figure 4 and are indicative of local disorder, could be a result of the non-stoichiometric phase of ZrO\(_2\) and a poorly crystallized Zr\(^{4+}\) and Sc\(^{3+}\) structure. To conclude, thin films at small deposition rates are of a mixed phase (\(m\)-ZrO\(_2\)), (\(t\)-ZrO\(_2\)).

### Table 2. The ratio of cubic, tetragonal and monoclinic phases in the ScAlSZ thin films.

| Deposition Rate (nm/s) | Substrate Temperature (°C) |
|------------------------|----------------------------|
|                        | 300 | 600 | 300 | 600 | 300 | 600 |
| Monoclinic             |     |     |     |     |     |     |
| 0.2                    | 35% | 28% | 65% | 72% | 0%  | 0%  |
| 0.4                    | 19% | 12% | 81% | 88% | 0%  | 0%  |
| 0.8                    | 6%  | 54% | 41% | 46% | 53% | 0%  |
| 1.2                    | 19% | 20% | 26% | 26% | 55% | 53% |
| 1.6                    | 19% | 18% | 26% | 23% | 55% | 59% |
| Tetragonal + Rhombohedral |   |     |     |     |     |     |
| 0.2                    |     |     |     |     |     |     |
| 0.4                    |     |     |     |     |     |     |
| 0.8                    |     |     |     |     |     |     |
| 1.2                    |     |     |     |     |     |     |
| 1.6                    |     |     |     |     |     |     |
| Cubic                  |     |     |     |     |     |     |
| 0.2                    |     |     |     |     |     |     |
| 0.4                    |     |     |     |     |     |     |
| 0.8                    |     |     |     |     |     |     |
| 1.2                    |     |     |     |     |     |     |
| 1.6                    |     |     |     |     |     |     |

**Figure 5.** Raman spectra of 6ScAlSZ thin films deposited on Alloy 600 substrates using (a) 300 °C and (b) 600 °C substrate temperature and different deposition rates from 0.2 to 1.6 nm/s.
4. Conclusions

Thin films of scandia alumina stabilized zirconia were formed using the e-beam physical vapor deposition method. Pellets for the deposition process were prepared from the powders of $\text{(Sc}_2\text{O}_3)_{0.06} (\text{Al}_2\text{O}_3)_{0.01} (\text{ZrO}_2)_{0.93}$. The crystalline structure of powders was polymorphic. Monoclinic, cubic and rhombohedral phases were identified using XRD and Raman methods. Deposited thin films had a different structure and chemical composition in comparison to powders of 6ScAlSZ. The concentrations of $\text{O}_2$, $\text{Al}$, $\text{Sc}$ and $\text{Zr}$ were $52.0 \pm 1.5$, $10.2 \pm 4.2$, $5.4 \pm 1.8$, and $32.6 \pm 2.5$ at.% respectively. It was found that the Al concentration in thin films was related to the deposition parameters, i.e., deposition rate and substrate temperature. The concentration of Al was lower using a higher deposition rate, and slightly higher using a higher substrate temperature. The XPS measurements revealed that the surface of thin films consists of $\text{Sc}$, $\text{Zr}$, $\text{Al}$ and $\text{C}$ compounds, oxygen vacancies and OH groups. The existence of $\text{ZrO}_2$ and oxygen vacancies, a high concentration of $\text{Al}_2\text{O}_3$ and metallic $\text{Al}$ affected the structural properties of thin films. The crystallinity of the thin films was made greater using a higher deposition rate and deposition temperature. In other words, the crystallinity was directly related to the aluminum concentration and the substrate temperature. It was also found that thin films are polymorphic. Raman analysis revealed that thin films consist of monoclinic, tetragonal, cubic, and small amounts of rhombohedral phases. Moreover, the amount of cubic phase was higher and the amount of tetragonal phase was lower using a higher deposition rate. Hence, a high concentration of $\text{Al}$ in the thin films suppresses the formation of the cubic phase. The most optimal conditions for obtaining thin films with the most stabilized cubic structure were obtained at high substrate temperatures and high deposition rates.

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