Photo-excitation effects on oxide-ion conductors: case study of zirconia thin films

Investigators

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Abstract

Enhanced grain growth in ultra-thin yttria-doped-zirconia (YDZ) films synthesized under ultraviolet (UV) irradiation is reported. The mean grain size in UV-activated 7.5 mol % yttria doped zirconia films nearly 56 nm thick increased to 85 nm upon annealing in an oxygen-rich ambient at 900 °C for one hour, while in thermally grown YDZ they grew only to ~15 nm under identical annealing conditions. In-situ electron microscopy kinetic studies reveal an enhanced kinetic constant and a self-limiting grain growth behaviour in the UV-synthesized oxide films.

Introduction

Ultraviolet (UV)-photon-assisted oxide film synthesis has gained prominence in recent years owing to its unique features such as the ability to produce films with superior crystallinity [1], atomically-tailored stoichiometry [2], and enhanced oxidation rates at low temperatures [3]. The proximity of the photon energy to the bond energy of the oxygen molecule introduces photochemical reactions that create activated oxygen species, thereby enabling enhanced kinetics of oxygen transport. Recently we have shown that UV-assisted oxidation is an attractive route to synthesize ultra-thin yttria-doped zirconia (YDZ) films with controlled interfacial layers on semiconductor substrates [4]. The result indicates that UV oxidation may be an attractive route to manipulate non-stoichiometry of oxide thin films even in extrinsically doped zirconia films. While several of these studies discuss changes in anion-related kinetics under UV irradiation, very little is known about the effect of photon irradiation on cation kinetics such as grain growth. Recent interest in alternate energy technologies such as low-temperature solid-oxide fuel cells has created a need for high-quality functional oxide thin films with a controlled microstructure [6]. However, grain growth in thin films can be markedly different from that observed in the bulk [7, 8], making detailed understanding of microstructure essential, along with innovative processing routes to control film morphology. In addition, previous studies on oxide ceramics indicate the grain boundary mobility is extremely sensitive to defects at grain boundaries. A study of the kinetics of grain growth could therefore be an excellent way to investigate defects in oxide thin films [9, 10, 11]. Significant grain growth enhancement was observed in 7.5 mol% yttria-doped zirconia films synthesized under UV irradiation (referred to as UV 7.5% YDZ), while almost no change was observed in YDZ films at high yttria doping (>10 mol %) or in undoped zirconia films. Our results suggest that cation-related kinetics in zirconia can be changed by a combination of aliovalent doping and oxygen point-defect concentration modulation via photon irradiation. It is important to note that cation mobility is primarily the rate-controlling step for grain boundary migration at nearly all compositions in fluorite-structured oxides [5].
**Background**

Synthesis of fuel cells via thin film routes has been gaining attention recently. Further, oxygen reduction mechanisms at electrodes, particularly the cathode is of great importance. This can affect the performance of fuel cells in the low and intermediate temperature range. Although scaling the electrolyte thickness can provide some advantages, it is important to understand catalytic phenomena at the cathode-electrolyte interfaces and our studies can provide fundamental understanding of the nature of oxidation and oxygen transport at oxide hetero-interfaces.

**Experimental**

In this study, we have used a custom-designed sputtering system fitted with a load-lock chamber capable of in-situ UV oxidation experiments under controlled oxygen partial pressure and temperature. Substrates were cleaned by acetone and ethanol for 5 minutes respectively, and then treated with buffered HF (2 %) for 2 minutes followed by de-ionized water cleaning before loading into the chamber. Zr-Y metal alloy films were grown by magnetron co-sputtering on Si (100) substrates at room temperature in a sputtering main chamber. The composition of Zr/Y was controlled by changing the growth parameters, including the power of the sputtering gun during deposition. After ~ 3-4 nm of Zr-Y precursor alloy were grown on the substrates, the samples were transferred to a load-lock chamber and oxidized under UV irradiation for 15 minutes at room temperature in 100 % O₂ ambient at ~ 1 atm. The resultant oxide thickness was ~ 5 nm, which correspond to the self-limiting thickness of Zr metal thin films at room temperature grown under UV [12]. A low-pressure Hg lamp with primarily wavelengths of 254 nm and 185 nm was used as a UV source in this study. The intensity of the light at a wavelength of 254 nm was ~ 17 mW/cm² and the distance between samples and the lamp was ~ 4 cm. More information on the spectrum of the low-pressure Hg lamp, the absorption coefficients of O₂ in the UV, and the photochemical reaction rates can be found elsewhere [13].

After UV oxidation, the load-lock chamber was immediately pumped down to ultra-high vacuum (reached < 5 × 10⁻⁵ mbar within 90 s) and the samples were transferred back into the main chamber for further growth. This process was repeated up to 10 times, followed by post-deposition UV irradiation for 1 hour in air. The total thickness of all samples reported in this study are nearly identical; ~ 56 ± 3 nm. The Y/Zr ratio was controlled by changing the growth parameters during the deposition. The crystal structure of as-grown (i.e., room-temperature) UV-grown YDZ film is cubic, while the tetragonal/monoclinic phase is formed in the as-grown undoped zirconia. The grain size at room temperature was ~ 10 nm with little dependence on the yttria concentration. Further details of the sample preparation procedure and as-grown morphology have been reported elsewhere [4]. Post growth annealing was conducted in 20 % O₂ + 80 % N₂ ambient at 900 °C for 1 hour, unless otherwise noted in the manuscript. To compare the results with films grown by other techniques, zirconia films of comparable thickness were also grown by thermal oxidation of Zr-Y alloy in the same ultra-high vacuum system as well as by RF sputtering of 8 mol% YDZ ceramic targets. Thermally grown films were prepared by dc co-sputtering of Zr-Y targets, followed by annealing in 20 % O₂ + 80 % N₂ ambient at 900 °C for 1 hour. The total deposition time, deposition rate, and resultant oxide thickness of thermally grown films were identical to the UV grown films, which enables us to investigate directly the effect of photon irradiation. RF sputtering of YDZ ceramic targets were also performed in the same sputtering system at a growth rate comparable to that of the Zr-Y alloy deposition for UV/thermally grown YDZ films. Film microstructure was investigated by a JEOL 2100 transmission electron microscopy (TEM). TEM specimens were prepared by mechanically thinning followed by Ar⁺ ion-beam milling. Grain size was determined by the linear intercept method [14]. Ions and defects are represented using the Kröger-Vink notation [15].
Results and discussion

1. Grain growth in thermally grown and UV grown un-doped zirconia

Figure 1 shows a plan-view TEM bright-field micrograph of thermally grown and UV-grown undoped pure zirconia after annealing at 900 °C. The grain size in thermally grown film (~ 20 nm) was slightly larger than that in the UV-grown film (~ 16 nm). Grain boundaries can function as sinks for oxygen vacancies ($V_{O}^{***}$) owing to their small formation energy. In fluorite-structured oxides, this excess of oxygen vacancies at grain boundary cores has been demonstrated both from theoretical calculations and experiments, and considered an important factor in determining the electrical properties of nanocrystalline materials [16]. In pure ZrO₂, the grain growth is typically controlled by the mobility of cation ions (Zr), which diffuse via a vacancy mechanism ($V_{Zr}^{m''}$ or ($V_{O}^{**}$+$V_{Zr}^{m''}$)) [17,18]. These charged cation-vacancy-related defects are attracted to the grain boundaries when they are positively charged due to excess oxygen vacancies, and their mobility is thereby slightly assisted. On the other hand, charged oxygen species may be supplied by photochemical reactions in the gas phase under UV irradiation, whereby oxygen vacancies at grain boundaries may be compensated, resulting in a near-neutral grain boundary charge state. Grain growth could therefore be predominantly controlled by Zr-vacancy diffusion without any assistance from ionic charges, resulting in a slightly slower grain growth than in thermally grown films. The report of nearly atomically uniform oxygen stoichiometry in crystalline pure ZrO₂ films grown under UV supports this hypothesis [2].

2. Grain growth in thermally grown and UV grown 7.5 % yttria doped zirconia

Figure 2 shows a TEM bright-field image of (a) a thermally grown and (b) a UV grown 7.5 % YDZ film. A significant difference in grain size is clearly seen from a comparison of the micrographs. Selected-area diffraction (SAD) patterns shown in the insets confirm the randomly oriented grain structure. Since both films were synthesized identically apart for room-temperature UV exposure in an oxygen-rich ambient in one case, these images indicate that the grain growth can be changed by UV irradiation of YDZ films. The average grain size of UV 7.5 % YDZ film was ~ 85 nm, which is nearly 1.5 times the film thickness, while the thermally grown 7.5 % YDZ film has an average grain size of ~ 15 nm. We also found that RF-sputtered 8 mol% YDZ films after annealing at 900 °C have an almost identical average grain size (~ 15 nm) as the thermally grown films.

In alio-valent doped zirconia, the number of point defects is predominantly extrinsically controlled. Yttrium (Y³⁺) ions occupy zirconium (Zr⁴⁺) sites and create charge-compensating oxygen vacancies according to the following reaction: $Y_{2}O_{3} = 2Y_{Zr}^{'''} + V_{O}^{***} + 3O_{2}^{x}$. Atomic-scale analysis of grain boundaries in YSZ has shown that there is an increase in the number of oxygen vacancies ($V_{O}^{***}$) in the grain boundary core, leading to a segregation of Y atoms ($Y_{Zr}^{'''}$) that balance charges [19]. This dopant segregation plays an important role in controlling grain growth owing to a solute-drag effect [5] and minimizing the strain caused by the difference in ionic radius between Y³⁺ (1.015 Å) and Zr⁴⁺ (0.84 Å). On the other hand, negatively charged oxygen interstitials may compensate oxygen vacancies at grain boundaries under photon irradiation, in a similar way to that described earlier. We have recently reported that the oxygen diffusivity in 7.5 % YDZ film grown under UV irradiation was almost the same as that in undoped zirconia, which suggests that oxygen-vacancy compensation takes place in UV-grown YDZ films [4]. On account of this charge compensation and the correspondingly suppressed grain boundary segregation, a large amount of aliovalent dopants ($Y_{Zr}^{'''}$) may exist
in the grain interior, making these cation defects unstable owing to strains from ionic radii difference and altered electro-neutrality condition.

It is interesting to note that the grain size of the same UV 7.5 % YDZ film annealed in extremely low partial pressure of oxygen \( (\text{Po}_2 \sim 10^{-17} \text{ atm at 900 } ^\circ\text{C}) \) was smaller than the one annealed in an oxygen-rich ambient. The oxygen partial pressure in the high-temperature furnace was controlled using water-hydrogen-oxygen equilibria. The average grain size after 900 °C annealing for 1 h in a low \( \text{Po}_2 \) was \( \sim 30 \text{ nm} \), while that in the sample annealed in oxygen-rich condition was \( \sim 85 \text{ nm} \). The oxygen reduction reaction
\[
O_o^x = \frac{1}{2} O_2 + V_o^{**} + 2e^- \text{ takes place below } \text{Po}_2 \sim 10^{-8} \text{ atm at 900 } ^\circ\text{C} \] [20]. This oxygen reduction reaction allows oxygen-vacancy creation and segregation at grain boundaries; therefore, segregation of Y dopants can take place under low \( \text{Po}_2 \). The Y segregation can relax the strain energy; resulting in a smaller grain size.

The UV 7.5 % YDZ sample was annealed *in-situ* in the TEM to investigate further the grain growth kinetics. From *in-situ* TEM heating experiments, we found that mean grain size rapidly changed from 15 nm to 80 nm at 700 °C within 30 minutes and that growth was almost suppressed after this rapid transition was completed as shown in Fig 3. The inset figure shows the evolution of the microstructure with respect to temperature where the sample was heated at 10 °C / min. After the grain size reached a self-limiting value of \( \sim 85 \text{ nm} \), no further significant grain growth was observed even at 800 °C, which agrees with reported grain-growth phenomena in thin films [21]. This self-limiting grain growth and weak temperature dependence on the limited grain size was also confirmed by *ex-situ* annealing in 20 % \( \text{O}_2 \). The grain size in films annealed at 800 °C and 900 °C for 3 h and 6 h were both \( \sim 85 \text{ nm} \). Grain growth kinetics typically follow the relation \( d^n - d_0^n = K_n t \), where \( d \) is the average grain size, \( d_0 \) is the grain size at \( t = 0 \), \( K_n \) is the kinetic constant of with grain-growth exponent \( n \), and \( t \) is the time [22]. If grain growth is controlled by surface curvature and grain boundary diffusion, the grain growth exponent \( n \sim 2 \), while \( n \sim 3 \) is commonly observed in the case of solute-drag-controlled grain growth [23]. From a fitting of \( d^n - d_0^n \) vs \( t \), the grain growth kinetic constant was determined to be \( K_2 = 2.82 \times 10^{-18} \text{ m}^2/\text{s} \) (for \( n = 2 \)) and \( K_3 = 2.35 \times 10^{-25} \text{ m}^3/\text{s} \) (for \( n = 3 \)) from the above analysis. The grain boundary mobility (\( M_{gb} \)) can be related to grain boundary diffusivity (\( D_{gb} \)) through the Nernst-Einstein equation
\[
D_{gb} = kT M_{gb} \delta / \Omega ,
\]
where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( \delta \) is the grain boundary thickness and \( \Omega \) is the atomic volume [15]. Using \( M_{gb} = K_n / n \gamma_{gb} d^{n-2} \) where \( \gamma_{gb} \) is the grain boundary energy and \( d \) is the grain size [15], and substituting \( \gamma_{gb} = 0.87 \text{ J/m}^2 \) [24], \( \delta = 0.5 \text{ nm}, \Omega \sim 3.39 \times 10^{-29} \text{ m}^3 \) [25] into above equations we can obtain \( D_{gb} = 3.21 \times 10^{-19} \text{ m}^2/\text{s} \) for \( n = 2 \) and \( D_{gb} = 3.33 \times 10^{-19} \text{ m}^2/\text{s} \) for \( n = 3 \) at \( d = 30 \text{ nm} \), which is comparable to the Y dislocation-pipe diffusivity at 700 °C extrapolated from data in Ref [26]. Estimation of diffusivity based on self-limiting behaviour
\[
D = (d_l - d_o)^i / 4 \tau_1,
\]
where \( D \) is the chemical diffusivity of solutes, \( d_l \) is the limited grain size, \( d_o \) is the grain size at \( t = 0 \), and \( \tau_1 \) is the relaxation time of the self-limiting growth [21, 27], also gives a nearly identical value. In UV 7.5 % YDZ films, a large amount of Y atoms residing in the grain interior may provide extra strain energy and it may be possible that strain relaxation through Y redistribution initiates rapid grain growth in these films. It is interesting to note that an enhanced kinetic constant has been reported previously for grain growth under stress in Y-doped zirconia [28].
3. **Grain growth in thermally grown and UV grown 11.3 % yttria doped zirconia**

Figure 4 shows TEM dark-field micrographs of (a) thermally grown and (b) UV-grown 11.3 % YDZ. The grain size was nearly identical (~ 15 nm) in both cases. This could be due to the fact that the amount of oxygen vacancies created by extrinsic Y doping exceeds the oxygen incorporation through UV-activated process in these films. Then grain growth may be predominantly controlled by space-charge-induced solute-drag effect. This solute drag suppression on grain growth was clearly seen in thermally grown films, where the grain size after 900 °C, 1 h annealing was 15 nm in 11.3 % YDZ, while it was 20 nm in undoped zirconia. This is also supported from our previous work [4] where we showed that oxygen diffusivity in UV 11.3 % YDZ was higher than in the 7.5 % thermally grown YDZ films. These results indicate UV oxidation can incorporate oxygen species in doped zirconia films and introduce dramatic changes in cation mobility likely through modulation of grain-boundary defect chemistry.

**Progress**

We found that grain growth in ultra-thin yttria-doped-zirconia (YDZ) film structures synthesized under ultra-violet (UV) irradiation is uniquely different from that in thermally grown films or RF-sputtered films, indicating cation kinetics can be manipulated by using UV irradiation. In undoped zirconia, the grain size of UV-grown films after high-temperature annealing is slightly smaller than thermally grown films. On the other hand, significant grain growth was found in UV-grown 7.5 mol % yttria doped zirconia annealed in an oxygen rich ambient at 900 °C; the grain size increased to 85 nm upon annealing, while in thermally grown YDZ of identical composition the grains grew to only ~15 nm under identical annealing. From in-situ studies on kinetics of grain growth, the UV-grown 7.5 mol % yttria doped zirconia films reveal an enhanced kinetic constant, corresponding to Y diffusivity via grain boundary or pipe diffusion. This enhanced grain growth was self-limited to ~ 85 nm, confirmed by ex-situ and in-situ annealing. The grain size of UV 7.5 % YDZ film annealed in extremely low Po2 was smaller than in the one annealed in an oxygen-rich ambient. We anticipate that these results could open an important route utilizing photon irradiation to control structure-property relations in oxide thin films.

**Relevant Publications**


**Future Plans**

We plan to investigate photo-excitation effects in complex oxides using in-situ instrumentation that we are presently setting up. Conductivity studies will be performed at high temperatures under activated conditions,
as well as chemical surface exchange studies (from conductivity relaxation) will be performed on such oxide films using a custom-designed small volume probe station. We anticipate these results to be of direct relevance to improving energy technologies such as fuel cells.

References

[25] The average atomic volume calculated from density and molar weight in JCPDF # 301468 (Zr0.85Y0.15O1.93).

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Figure 1:
TEM plan-view micrograph of thermally grown and UV-grown zirconia thin films after annealing at 900 °C in 20 % O₂ for 1 hour. (a) Thermally grown undoped ZrO₂ (b) UV-assisted undoped ZrO₂. High-resolution image shows distinct grain boundary with no amorphous phases.

Figure 2:
TEM plan-view micrograph of (a) thermally grown and (b) UV-grown YDZ 7.5 % thin films.

Figure 3:
Grain size evolution during isothermal annealing and corresponding dark-field TEM images of UV-grown YDZ 7.5 % thin film. The sample was annealed in-situ inside the TEM at 700 °C. The inset figure shows grain size as a function of annealing temperature.

Figure 4:
TEM plan-view dark-field images of (a) thermally grown and (b) UV-grown 11.3 % YDZ thin films.
Figure 2

Figure 3
Figure 4