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# Oxidant effect of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution on the crystalline characteristics of nanocrystalline $\text{ZrO}_2$ films grown by atomic layer deposition



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## ABSTRACT

Nanocrystalline  $\text{ZrO}_2$  films were synthesized by atomic layer deposition method using  $\text{CpZr}[\text{N}(\text{CH}_3)_2]_3$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ) as the metal precursor and  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution as the oxygen source. La element in the deposited  $\text{ZrO}_2$  films could not be detected as its content was below the resolution limit of the X-ray photoelectron spectroscopy. The alternative introduction of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution to conventionally used  $\text{H}_2\text{O}$  as the oxidant effectively altered the crystalline structure, grain size, and surface roughness of the grown  $\text{ZrO}_2$  films. Specifically, the crystalline structure of the  $\text{ZrO}_2$  film changed from a mixture of tetragonal and monoclinic phases to monoclinic phase. The average grain size also increased, and the resulting film surface became rougher. The average grain sizes of the  $\text{ZrO}_2$  films prepared from  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution at concentrations of 10, 20, 30, and 40% were 280, 256, 208, and 200 nm, respectively, whereas that prepared using  $\text{H}_2\text{O}$  oxidant was 142 nm. However, the concentration of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution minimally influenced the crystalline characteristics of the nanocrystalline  $\text{ZrO}_2$  films i.e., the crystalline structure, grain size, and surface roughness except for crystallite size.

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## 1. Introduction

Zirconium oxide ( $\text{ZrO}_2$ ) thin films have been commonly used as dielectric layers in metal–insulator–metal capacitors, charge trapping layers in non-volatile flash memory devices, and insulating layers in resistive switching memory devices owing to their high dielectric constant ( $\kappa$ ) and good insulating property [1]. For application in the aforementioned semiconductor devices, the  $\text{ZrO}_2$  film on the semiconductor or metal substrate needs to be either amorphous or crystalline as required by the target applications. Crystalline  $\text{ZrO}_2$  films feature higher  $\kappa$  values but undesirable larger leakage currents occurring through the grain boundaries when compared

with amorphous  $\text{ZrO}_2$  films which characterize lower  $\kappa$  values but desirable lower leakage currents.

Furthermore, nanocrystalline  $\text{ZrO}_2$  films with different crystalline phases, such as monoclinic, tetragonal, and cubic, have been widely applied as catalysts [2,3], as bioactive coating materials [4], in optics [5], as solid electrodes in fuel cells [6], and as nanolaminated scaffolds in encapsulation technologies [7]. In most of the applications mentioned above, modification of the crystalline characteristics of thin film nanostructures, such as crystallite size, grain size, and their distribution, strongly influence the performance of the films [8]. For instance, an inverse correlation between the band gap and crystallite size of  $\text{ZrO}_2$  films grown by sputter deposition method was determined i.e., the band gap energy, which was evaluated from transmittance spectra, increased from 5.78 to 6.07 eV with reducing crystallite sizes from 20 to 7 nm [8]. Additionally, surface modification of thin film nanostructures plays a determining role in enhancing the efficiency of solar cells [9].

Nanocrystalline  $\text{ZrO}_2$  films have been prepared by atomic layer deposition (ALD) method [10–14]. ALD is a leading nano-scale film deposition method that has been commonly employed in various

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nano-device fabrications. In the ALD process, the vaporized precursor and reactant are alternately supplied onto each substrate surface, and the film grows by successive reactions of precursor and reactant with the substrate surface. In the fabrication of binary metal oxide films, the complete cycle of ALD for the formation of a monolayer typically consists of four steps: (1) pulsing with metal precursor; (2) purging with inert gas; (3) pulsing with oxidant; and (4) purging with inert gas. The precursor and oxidant alternately supplied at steps (1) and (3) should be well isolated by the purging process to promote surface-phase reactions and prevent gas-phase reactions.

To fabricate metal oxide films using ALD, the choice of both the metal precursor and oxidant is very important for a successful ALD process. Various oxidants have been reported such as H<sub>2</sub>O [15], H<sub>2</sub>O<sub>2</sub> [16], O<sub>2</sub> [17], O<sub>3</sub> [18], plasma-based radical oxygen [19], and metal alkoxides [20]. The oxidant can change the characteristics of the deposited films such as the thickness of the interfacial layer [20], electrical properties [21], and growth rate [21]. For instance, by using a metal alkoxides (e.g., aluminum isopropoxide) as the oxidant, the formation of interfacial SiO<sub>2</sub> layer can be prevented during the deposition of an Al<sub>2</sub>O<sub>3</sub> layer on a Si substrate via ALD [20].

Besides the influence of the metal precursor and oxidant on the ALD process, the introduction of another compound such as a catalyst in the ALD process can afford low-temperature deposition of metal oxides [22]. For instance, the ALD of SiO<sub>2</sub> can be conducted at low temperatures, even at room temperature, in the presence of an amine ligand (NH<sub>3</sub><sup>-</sup>) that catalyzed nucleophilic attacks of SiCl<sub>4</sub> by hydroxyl oxygens. Of interest, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O has been commonly used as a starting material for preparing new compounds in various application fields [23]. For example, LaCoO<sub>3</sub> can be prepared from La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, whereby the aqueous nitrate state of lanthanum is used to eliminate the water molecules and NO<sub>3</sub><sup>-</sup> ions, resulting in the formation of pores in the bulk material. Additionally, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O has been used as an additive to enhance its adsorption affinity for phosphorus [24]. In another example, introducing La<sup>3+</sup> in mesoporous TiO<sub>2</sub> photocatalyst can reduce the amount of defective –OH groups on the catalyst surface [25]. As La-based materials have been used as an additive to either enhance the reactivity or modulate the material characteristics in numerous material fabrication processes, it is expected that La-based oxidants in ALD process can also influence the crystalline and morphological properties of nanocrystalline ZrO<sub>2</sub> films. However, it is rare to purposely alter the nanocrystalline properties of ZrO<sub>2</sub> films using common and conventional processing conditions in ALD process, except for oxidant specimen.

Accordingly, in this study, nanocrystalline ZrO<sub>2</sub> films were fabricated by ALD using the CpZr[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (Cp = C<sub>5</sub>H<sub>5</sub>) precursor and the oxidant La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution instead of conventional H<sub>2</sub>O in order to vary the crystalline characteristics of ZrO<sub>2</sub> films. To investigate the effect of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution oxidant on the crystalline properties of the deposited ZrO<sub>2</sub> films, the concentration of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution was varied from 0 to 40% (a La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O concentration of 0% implies that H<sub>2</sub>O acted as the sole oxidant). The crystalline characteristics i.e., crystalline phase, crystallite size, grain size, and surface roughness were evaluated by grazing incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

## 2. Experimental

### 2.1. Nanostructure ZrO<sub>2</sub> thin film deposition

Nanocrystalline ZrO<sub>2</sub> films were deposited on Si(100) substrates by ALD method using CpZr[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub> as the metal precursor and

La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution or H<sub>2</sub>O as the oxygen source. Prior to the deposition process of ZrO<sub>2</sub>, the p-type (1–10 Ω cm) Si substrates were cleaned in a dilute HF solution (~1% HF in deionized water) for 2 min to remove native oxides, then rinsed with deionized water, and finally dried with N<sub>2</sub> gas. The cleaned substrates were then introduced into the showerhead-type thermal ALD chamber and left in inert Ar environment for 30 min for thermal stability. Subsequently, the ALD process was initiated. The metal precursor, CpZr[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, was vaporized at 65 °C and introduced into the chamber using Ar carrier gas (>99.999%). Additionally, to avoid condensation of the vaporized precursor, the supply line linked to the ALD reactor was maintained at 105 °C in all processes. The liquid oxidant, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution or H<sub>2</sub>O, was vaporized at room temperature, and the vaporized oxidant was delivered to the chamber without any carrier gas. La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solutions at varying weight concentrations of 10, 20, 30, and 40% were prepared and used for sample preparation. The vapor pressure of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solutions was measured using a static method at 30 °C and ranged at 35–37 torr which is similar to that (36 torr) of H<sub>2</sub>O. Five types of ZrO<sub>2</sub> films were obtained using H<sub>2</sub>O and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solutions at four different concentrations as oxidants. The same process parameters were used for all films as follows. A cycle of ALD consisted of four steps: (1) pulsing with CpZr[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub> with Ar carrier gas for 4.5 s; (2) purging with Ar gas for 10 s; (3) pulsing with either H<sub>2</sub>O or La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution for 5 s; and (4) purging with Ar gas for 10 s. The ZrO<sub>2</sub> film growth was performed for 500 cycles at 300 °C.

### 2.2. Analyses of nanostructure ZrO<sub>2</sub> thin films properties

To analyze the chemical binding of the ZrO<sub>2</sub> films and determine the presence of La element in the deposited ZrO<sub>2</sub> films, X-ray photoelectron spectroscopy (XPS; Theta Probe AR-XPS System, Thermo Fisher Scientific, detection limit is 0.1 at.%), was employed using an Al Kα X-ray source. The obtained XPS peaks were fitted using a Tougaard background and a Voigt (mixed 20% Lorentzian and 80% Gaussian) line shape. The crystalline and morphological properties of the ZrO<sub>2</sub> films were investigated using GIXRD, SEM, and AFM. The phase composition and average crystallite size were evaluated using GIXRD (Rigaku). The average grain size and root-mean-square (RMS) roughness were respectively determined by SEM (Hitachi-S4800) and AFM (Park system).

## 3. Results and discussion

### 3.1. XPS analysis and chemical status

Fig. 1 shows the Zr 3d, O 1s, and La 3d XPS spectra of the crystalline ZrO<sub>2</sub> films deposited using H<sub>2</sub>O and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution at varying concentrations. No major differences in the survey XPS scans of Zr 3d and O 1s in Fig. 1a and b of the films prepared at different concentrations of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution were observed aside from the slight shift in the peak position for the film prepared at 30% La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O that is within the error measurement range.

Specially, the Zr 3d XPS spectra of the ZrO<sub>2</sub> films prepared with H<sub>2</sub>O oxidant and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solutions featured two main spin-orbit doublets at 182.0 ± 0.2 eV (3d<sub>5/2</sub>) and 184.3 ± 0.1 eV (3d<sub>3/2</sub>) (Fig. 1a). Regardless of the oxidant type or concentration, the splitting between the two main peaks ranged from 2.33 to 2.37 eV. Additionally, the intensity ratio of the Zr 3d<sub>5/2</sub> and Zr 3d<sub>3/2</sub> peaks for all the films prepared was approximately 3:2, which corresponds to the theoretical ratio, indicating the presence of Zr<sup>4+</sup> ions [26]. Thus, the results indicate that the ZrO<sub>2</sub> films fabricated with La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution are stoichiometric in accordance to literature values [27,28].

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