

# Preparation of Ti, Ta, Zr-based Oxide Films by Laser Chemical Vapor Deposition

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## Outline of the thesis

### Chapter 1 Introduction

In this thesis, I introduce the background of our research and emphasize the importance and applicability of three perovskite systems, including Sr–Ti–O, Na–Ta–O and Sr–Zr–O.

As we know that the ever growing carbon dioxide (CO<sub>2</sub>) emission is leading our race to a shortly-irretrievable warmer atmosphere. The increasing demand of energy is sending us an urgent signal to develop more efficient materials to support our society. However, a large portion of the energy we are using are from traditional fossil fuels. It seems more necessary than any time for us to develop more efficient and stable clean energies before it is too late to remediate. Thus, finding various paths to generate electricity and storage them to support our society, minimizing our dependence on traditional fossil fuels, and mitigating the risks of climate change should be prudent methods.

Oxide compounds from Sr–Ti–O, Na–Ta–O and Sr–Zr–O systems have been known for decades. they commonly possess excellent electrical properties and can be widely applied for photoelectrochemical conversion. In my study, I designed the laser chemical vapor deposition (LCVD) method to study the preparation of Sr–Ti–O, Na–Ta–O and Sr–Zr–O compounds and their photoelectrochemical properties. The deposition temperature on phase formation, microstructure and deposition rates were also investigated.

### Chapter 2 Preliminary investigation

In this chapter, a thorough literature survey of the Sr–Ti–O, Na–Ta–O and Sr–Zr–O systems was conducted. The pioneering works and recent advances of these three system were concluded, respectively. Moreover, properties of each individual perovskite oxide compound were introduced.

First, Sr–Ti–O system is comprised of TiO<sub>2</sub>, SrTiO<sub>3</sub> and Sr<sub>n+1</sub>Ti<sub>n</sub>O<sub>3n+1</sub> compounds. TiO<sub>2</sub> has anatase, rutile and brookite three phases, in which anatase and rutile are known as efficient photocatalysts along with their extraordinary dielectric properties. Anatase and rutile are wide bandgap semiconductors with bandgaps of 3.2 and 3.0 eV, respectively. Anatase phase is more stable than rutile TiO<sub>2</sub> with grain sizes smaller than 15 nm. Fujishima group paved the path and conducted the pioneering work of using anatase TiO<sub>2</sub> to be photocatalysts. Taking advantages of the electronic structure of it, solar energy can be captured to separate water to be hydrogen and oxygen. So far, anatase TiO<sub>2</sub> is still one of the most efficient photocatalyst to harvest hydrogen and remediate

environment. In contrast, rutile phase is more stable at bulk phase and are also widely studied. SrTiO<sub>3</sub> with a typical perovskite structure has also been exhibiting their advances no matter in the field of electrical ceramics, coatings or photocatalysts. SrTiO<sub>3</sub> possesses a similar bandgap of 3.2 eV. The perovskite structure of SrTiO<sub>3</sub> offers an opportunity for further modification through doping engineering. Sr<sub>n+1</sub>Ti<sub>n</sub>O<sub>3n+1</sub> is known as the ruddlesden-popper (RP) phase, including Sr<sub>4</sub>Ti<sub>3</sub>O<sub>10</sub>, Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> and Sr<sub>2</sub>TiO<sub>4</sub>, it is being a difficulty to prepare Sr<sub>4</sub>Ti<sub>3</sub>O<sub>10</sub>, Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> phases since they were reported to metastable at room temperature.

Second, Na–Ta–O system is mainly composed of Ta<sub>2</sub>O<sub>5</sub> and NaTaO<sub>3</sub> phases. Ta<sub>2</sub>O<sub>5</sub> has been reported to have excellent dielectric property, meanwhile it possesses a high refractive index and exhibits photoluminescence. Ta<sub>2</sub>O<sub>5</sub> films can be widely applied into dielectric devices, resistive random access memories and optical coatings. NaTaO<sub>3</sub> is also a wide bandgap (4.0 eV) semiconductor. Kudo group first investigated the photoactivity of NaTaO<sub>3</sub> compounds and proved the feasibility of enhancing their properties by tailoring the electronic structure. It is worth of noting that since Na<sup>+</sup> is highly volatile under elevated temperature, it is difficult for conventional methods to prepare NaTaO<sub>3</sub> films. Thus, LCVD can be applied to study Na–Ta–O system films.

Third, oxide compounds in Sr–Zr–O system generally have wider bandgaps. For example, the bandgaps of ZrO<sub>2</sub> and SrZrO<sub>3</sub> can reach 5.6–6.0 eV. Theoretically, even though it is believed to be controversial for the feasibility of photocatalysts. Previous experiments did show the defects, such as oxygen vacancies, can contribute to photoactivity of SrZrO<sub>3</sub>. The self-trapping phenomenon often can be observed in SrZrO<sub>3</sub> compounds, which can also give rise to photoluminescence. Besides, the high thermal stability and high ionic conductivity makes ZrO<sub>2</sub> applicable in abrasive additives, protective coatings, oxygen sensors and fuel cell membranes. The excellent dielectric property and potential photoactivity of SrZrO<sub>3</sub> renders its thin films to be suitable candidates for thin film capacitors, solar cells, self-cleaning coatings.

### Chapter 3 Preparation of TiO<sub>2</sub>-SrTiO<sub>3</sub> films

In this chapter, Sr–Ti–O films were prepared by using laser CVD. The effect of  $T_{\text{dep}}$  and Sr/Ti molar ratio on the composition of Sr–Ti–O compounds were investigated. TiO<sub>2</sub> films were prepared at Ti = 90–100 mol%,  $T_{\text{dep}}$  = 863–1003 K. Rutile TiO<sub>2</sub> films were prepared at lower  $T_{\text{dep}}$  = 863–913 K. Mixture of SrTiO<sub>3</sub> and TiO<sub>2</sub> were prepared at Ti = 67–90 mol%,  $T_{\text{dep}}$  = 843–983 K. Co-oriented structures of (001) anatase TiO<sub>2</sub> and (111)-SrTiO<sub>3</sub> were found Ti = 80 mol%,  $T_{\text{dep}}$  = 910 K and Ti = 83 mol%,  $T_{\text{dep}}$  = 920 K, respectively. Pure SrTiO<sub>3</sub> films were prepared at Ti = 50–90 mol%,  $T_{\text{dep}}$  = 843–983 K. Highly (111)-oriented SrTiO<sub>3</sub> films were prepared at Ti = 50 mol%,  $T_{\text{dep}}$  = 950 K and Ti = 57 mol%,  $T_{\text{dep}}$  = 957 K, respectively. Highly (110)-oriented SrTiO<sub>3</sub> films were prepared at Ti = 66 mol%,  $T_{\text{dep}}$  = 900 K and Ti = 62.5 mol%,  $T_{\text{dep}}$  = 900 K, respectively. Amorphous mixture of Sr<sub>4</sub>Ti<sub>3</sub>O<sub>10</sub>, SrTiO<sub>3</sub> and TiO<sub>2</sub> were mainly prepared at Ti = 50–80 mol%,  $T_{\text{dep}}$  = 840–900 K.

The (100)-oriented rutile TiO<sub>2</sub> film prepared at Ti = 100 mol%,  $T_{\text{dep}}$  = 823 K shows the worm-like surface grains and a dense cross-section. For the (101)-oriented anatase TiO<sub>2</sub> film prepared at Ti = 100 mol%,  $T_{\text{dep}}$  = 1003 K, a columnar cross-section with polygonal grains was found. The (001)-anatase TiO<sub>2</sub>/(111)-SrTiO<sub>3</sub> co-oriented film prepared at Ti = 83 mol%,  $T_{\text{dep}}$  = 920 K has an amorphous surface structure with granular grain and a dense cross-section. The (111)-oriented SrTiO<sub>3</sub> films show well-faceted triangular surface grains with columnar cross-sections. The (110)-oriented SrTiO<sub>3</sub> films show well-faceted prismatic grains with a columnar cross-section.

### Chapter 4 Epitaxial growth of SrTiO<sub>3</sub> films

In this chapter, SrTiO<sub>3</sub> films were epitaxially on (100) and (111) MgO, and (100) MgAl<sub>2</sub>O<sub>4</sub> substrates, respectively. Epitaxial (100)-oriented SrTiO<sub>3</sub> films were prepared on (100) MgO substrates at  $T_{\text{dep}}$  = 1123–1203 K. A low  $T_{\text{dep}}$  of 1023 K resulted in the formation of (111)-oriented SrTiO<sub>3</sub> films on (100) MgO substrates. A dense (100)-oriented SrTiO<sub>3</sub> film with a flat surface was epitaxially grown on a (100) MgO substrate with an in-plane

orientation at  $T_{\text{dep}} = 1203$  K. The in-plane orientation relations were  $\text{SrTiO}_3$  (100) //  $\text{MgO}$  (100) and  $\text{SrTiO}_3$  [100] //  $\text{MgO}$  [100]. The deposition rates of epitaxial (100)-oriented  $\text{SrTiO}_3$  films were  $18\text{--}32 \mu\text{m h}^{-1}$ . Epitaxial (111)-oriented  $\text{SrTiO}_3$  films were prepared on (111)  $\text{MgO}$  substrates at  $T_{\text{dep}} = 983\text{--}1063$  K. A high  $T_{\text{dep}}$  of 1113 K resulted in the formation of  $\text{SrTiO}_3$  film consisting of polygonal grains. Epitaxial (111)  $\text{SrTiO}_3$  films prepared at 983 K had a columnar structure with triangular pyramidal caps. The in-plane orientation relations were  $\text{SrTiO}_3$  (111) //  $\text{MgO}$  (111). The deposition rates of epitaxial (100)- and (111)-oriented  $\text{SrTiO}_3$  films were  $13\text{--}25$  and  $18\text{--}32 \mu\text{m h}^{-1}$ , respectively.

$\text{SrTiO}_3$  films were prepared on (100)  $\text{MgAl}_2\text{O}_4$  single-crystal substrates at  $T_{\text{dep}} = 983\text{--}1113$  K. (111)-oriented  $\text{SrTiO}_3$  film was obtained at  $T_{\text{dep}} = 983$  K and comprised columnar grains with triangular pyramidal caps. Epitaxial (100)  $\text{SrTiO}_3$  films were grown at  $T_{\text{dep}} = 1003\text{--}1113$  K. The in-plane orientation relation between epitaxial (100)  $\text{SrTiO}_3$  film and  $\text{MgAl}_2\text{O}_4$  substrate was (100)  $\text{SrTiO}_3$  // (100)  $\text{MgAl}_2\text{O}_4$  and [001]  $\text{SrTiO}_3$  // [001]  $\text{MgAl}_2\text{O}_4$ . The epitaxial (100)  $\text{SrTiO}_3$  film prepared at  $T_{\text{dep}} = 1113$  K showed a dense structure comprising nanosized columnar grains. The relative transmittance of the epitaxial (100)  $\text{SrTiO}_3$  film reached 95% at  $\lambda = 800$  nm. The deposition rate of the transparent (100)  $\text{SrTiO}_3$  film was  $20 \mu\text{m h}^{-1}$ .

## Chapter 5 Preparation of $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ films

In this chapter, mixture phases of  $\text{Sr}_4\text{Ti}_3\text{O}_{10}$  and  $\text{SrTiO}_3$  were obtained at  $\text{Ti} = 43\text{--}50$  mol%,  $T_{\text{dep}} = 883\text{--}1003$  K. Mixture phases  $\text{Sr}_3\text{Ti}_2\text{O}_7$  and  $\text{SrTiO}_3$  were obtained at  $\text{Ti} = 33\text{--}43$  mol%,  $T_{\text{dep}} = 883\text{--}1003$  K. Mixture phases of  $\text{Sr}_2\text{TiO}_4$  and  $\text{SrTiO}_3$  were obtained at  $\text{Ti} = 20\text{--}33$  mol%,  $T_{\text{dep}} = 853\text{--}1003$  K. (110)-oriented  $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ ,  $\text{Sr}_3\text{Ti}_2\text{O}_7$  and  $\text{Sr}_2\text{TiO}_4$  films were prepared at  $\text{Ti} = 33\text{--}50$  mol%,  $T_{\text{dep}} = 943\text{--}1003$  K. Well faceted surface morphologies are consisted of elongated roof-like grains. All the films showed columnar cross-sections. The roof-like structures of the (110)-oriented  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  films are associated with the {100} planes of tetragonal structure terminated by the (110) planes.

## Chapter 6 Preparation of $\text{Ta}_2\text{O}_5\text{-NaTaO}_3$ films

In this chapter,  $\text{Na-Ta-O}$  films were prepared by using laser CVD. The effect of  $T_{\text{dep}}$  and  $\text{Na/Ta}$  molar ratio on the composition of  $\text{Na-Ta-O}$  compounds were investigated.

$\text{Ta}_2\text{O}_5$  films were prepared at  $\text{Na} = 0\text{--}20$  mol%,  $T_{\text{dep}} = 793\text{--}1003$  K. *b*-axis and *c*-axis oriented  $\text{Ta}_2\text{O}_5$  films were prepared at  $\text{Na} = 0$  mol%,  $T_{\text{dep}} = 973$  K and  $\text{Na} = 0$  mol%,  $T_{\text{dep}} = 973$  K, respectively. With increasing  $\text{Na}$  supplying fraction, mixture of  $\text{Na}_2\text{Ta}_4\text{O}_{11}$  and  $\text{Ta}_2\text{O}_5$  were prepared at  $\text{Na} = 8\text{--}29$  mol%,  $T_{\text{dep}} = 883\text{--}1003$  K. Co-oriented structures of *c*-axis  $\text{Na}_2\text{Ta}_4\text{O}_{11}/(001)\text{-Ta}_2\text{O}_5$  film were found at  $\text{Na} = 0$  mol%,  $T_{\text{dep}} = 973$  K. Mixture of *c*-axis  $\text{Na}_2\text{Ta}_4\text{O}_{11}$  and (100)- $\text{NaTaO}_3$  film were prepared at  $\text{Na} = 29\text{--}44$  mol%,  $T_{\text{dep}} = 883\text{--}1003$  K. Another co-oriented mixture of *c*-axis  $\text{Na}_2\text{Ta}_4\text{O}_{11}/(100)\text{-NaTaO}_3$  were prepared at  $\text{Na} = 8\text{--}20$  mol%,  $T_{\text{dep}} = 853$  K. Pure  $\text{NaTaO}_3$  phase covers a wide range of  $\text{Na} = 29\text{--}90$  mol%,  $T_{\text{dep}} = 793\text{--}1003$  K. Mixed phase of  $\text{Na}_3\text{TaO}_4$  and  $\text{NaTaO}_3$  were also prepared at  $\text{Na} = 56\text{--}75$  mol%,  $T_{\text{dep}} = 793\text{--}1003$  K.

The *b*-axis oriented  $\text{Ta}_2\text{O}_5$  films showed the elongated prismatic surface morphology and dense cross-sections with jagged caps on the top. The highly *c*-axis oriented  $\text{Ta}_2\text{O}_5$  film showed a significantly different morphology with granular surface structure and a columnar cross-section. All the *c*-axis-oriented  $\text{Na}_2\text{Ta}_4\text{O}_{11}$  films showed hexagonal prismatic shaped surface grains with columnar cross-sections. The oriented *o*- $\text{NaTaO}_3$  films were prepared using laser CVD. The orientation of the *o*- $\text{NaTaO}_3$  films was changed from (101) to (112) to (001) plane as the increase of deposition temperature from 823 to 913 K. *o*- $\text{NaTaO}_3$  films had faceted surfaces and columnar cross sections. The deposition rates of *o*- $\text{NaTaO}_3$  films were  $48\text{--}120 \mu\text{m h}^{-1}$ , which are 192–6000 times higher than those offered by wet-chemical routes.

## Chapter 7 Preparation of ZrO<sub>2</sub>-SrZrO<sub>3</sub> films

In this chapter, Sr–Zr–O films were prepared by using laser CVD. The effect of  $T_{\text{dep}}$  and Sr/Zr molar ratio on the composition of Na–Ta–O compounds were investigated. Tetragonal ZrO<sub>2</sub> (t-ZrO<sub>2</sub>) films were prepared at Zr = 80 mol%,  $T_{\text{dep}} = 793\text{--}853$  K and Zr = 100 mol%,  $T_{\text{dep}} = 793\text{--}913$  K, respectively. With increasing Zr supplying amount, mixture of SrZrO<sub>3</sub> and ZrO<sub>2</sub> were prepared at Zr = 50–66 mol%,  $T_{\text{dep}} = 793\text{--}1003$  K. co-oriented structures of (101) t-ZrO<sub>2</sub> and (110)-SrZrO<sub>3</sub> were found Zr = 67 mol%,  $T_{\text{dep}} = 823$  K and 943 K, respectively. Pure orthorhombic SrZrO<sub>3</sub> films were prepared at Zr = 50 mol%,  $T_{\text{dep}} = 823$  and 883–943 K, respectively. Sr<sub>3</sub>Zr<sub>2</sub>O<sub>7</sub>, SrZrO<sub>3</sub> and SrO were found at the region of Zr = 33–44 mol%,  $T_{\text{dep}} = 823\text{--}1003$  K

The (101)-oriented t-ZrO<sub>2</sub> dominant film  $T_{\text{dep}} = 823$  K shows granular surface grains and a columnar cross-section. The m-ZrO<sub>2</sub> dominant films prepared at  $T_{\text{dep}} = 823$  K also shows granular surface structure however, the grain size changed to be much smaller. A columnar cross-section was also found for the m-ZrO<sub>2</sub> dominant film. The (101) t-ZrO<sub>2</sub>/(110)-SrZrO<sub>3</sub> co-oriented film prepared at Zr = 67 mol%,  $T_{\text{dep}} = 823$  K has a columnar cross-section with triangular faceted surface grains. The (101) t-ZrO<sub>2</sub>/(110)-SrZrO<sub>3</sub> co-oriented film prepared at Zr = 67 mol%,  $T_{\text{dep}} = 943$  K shows cauliflower-like surface grains and a columnar cross-section.

The orientations of o-SrZrO<sub>3</sub> films changed from (121) to (*h*21) as increasing  $T_{\text{dep}}$  from 883 to 943 K. The (121)-oriented o-SrZrO<sub>3</sub> film comprises a columnar cross-section with elongated roof-like surface grains, while that of (*h*21)-oriented o-SrZrO<sub>3</sub> films showed the triangular-shaped surface structure with a columnar cross-section. The maximum deposition rate of (*h*21)-oriented SrZrO<sub>3</sub> films reached 60  $\mu\text{m h}^{-1}$ .

## Chapter 8 Conclusion

Sr–Ti–O, Na–Ta–O and Sr–Zr–O systems were prepared by laser CVD. The photocatalytic activity for hydrogen evolution of SrTiO<sub>3</sub>, NaTaO<sub>3</sub> and SrZrO<sub>3</sub> films were investigated. The highest hydrogen evolution rate of the SrTiO<sub>3</sub> film reached 494  $\mu\text{mol g}^{-1} \text{h}^{-1}$ , corresponding to a calculated solar to a hydrogen efficiency of 0.09%. This is about 4.3 times higher than the SrTiO<sub>3</sub> powder prepared by solid-state method. The hydrogen evolution rate of the (001)-oriented o-NaTaO<sub>3</sub> film, 5672  $\mu\text{mol g}^{-1} \text{h}^{-1}$ , was 6 times higher than the (112)-oriented o-NaTaO<sub>3</sub> film and 3 times higher than the o-NaTaO<sub>3</sub> powder prepared by wet chemical route. The highest hydrogen evolution rate of the o-SrZrO<sub>3</sub> film reached 960  $\mu\text{mol g}^{-1} \text{h}^{-1}$ , and giving rise to a calculated solar to hydrogen efficiency of 0.29%. This is about 20 times higher than the SrZrO<sub>3</sub> powder prepared by solid-state method.

The study of the optical properties through UV-vis and PL measurements allowed us a deeper understanding about the light absorption process and the nature in transitions in the SrTiO<sub>3</sub>, NaTaO<sub>3</sub> and SrZrO<sub>3</sub> films, being favored the absorption in the films with direct transitions. The electrical features of the SrTiO<sub>3</sub>, NaTaO<sub>3</sub> and SrZrO<sub>3</sub> films determined by PEC characterization were correlated with the photocatalytic performance. The SrTiO<sub>3</sub>, NaTaO<sub>3</sub> and SrZrO<sub>3</sub> films showed high photocurrent density and charge carrier concentration. Finally, the hydrogen evolution rate of SrTiO<sub>3</sub>, NaTaO<sub>3</sub> and SrZrO<sub>3</sub> films prepared by LCVD ranges 3–20 times higher than those of traditional methods, which further proves that Ti-, Ta- and Zr-based films prepared by LCVD are promising candidates for photocatalytic materials.