

L-45

### Synthesized of Photocatalytic SrTiO<sub>3</sub> and CaTiO<sub>3</sub> Thin Film for Hydrogen Generation by Pulsed Laser Deposition

\*Masateru Saito<sup>1</sup>, Takayuki Kurihara<sup>2</sup>, Satoshi Kurumi<sup>3</sup> and Kaoru Suzuki<sup>3</sup>

SrTiO<sub>3</sub> and CaTiO<sub>3</sub> are photocatalytic material which could grow hydrogens from water and expect for hydrogen-fuel cells. The structure of these materials were perovskite which suits for water-splitting reaction. To apply the water-splitting reaction, photocatalytic material prefer thin film samples to powder or bulk samples because it was difficult to collect disrupt powder or bulk samples in water after the photocatalytic decomposition. SrTiO<sub>3</sub> and CaTiO<sub>3</sub> thin films were deposited by pulsed laser deposition. In this study, water-splitting gases which our growth samples could generate hydrogen gases; SrTiO<sub>3</sub> thin film was 11 μl/cm<sup>2</sup>h, CaTiO<sub>3</sub> thin film was 26 μl/cm<sup>2</sup>h.

#### 1. Introduction

Photocatalytic decomposition of H<sub>2</sub>O has been studied since the Honda-Fujishima effect was discovered by K. Honda and A. Fujishima<sup>[1]</sup>. TiO<sub>2</sub>/Pt electroad generated hydrogen and oxygen under irradiation ultraviolet light with Honda-Fujishima Effect. Photocatalyst generated electron and hole under irradiation light of more than there were energy gap which developed oxidation-reduction reaction on photocatalyst surface. In particular, Titania (TiO<sub>2</sub>) is widely used in photocatalyst due to strong oxidation power. Furthermore, photocatalyst by decompose water is expected to be a renewable energy source. The perovskite structure of SrTiO<sub>3</sub> and CaTiO<sub>3</sub> were investigated because it has higher water decomposition efficiency than that of titania<sup>[2][3]</sup>. In this study, pulsed laser deposition method was used as a photocatalytic thin film method. We investigated the characteristics of the thin film.

#### 2. Method

Figure 1 shows an experimental apparatus for the pulsed laser deposition (PLD). The SrTiO<sub>3</sub> and the CaTiO<sub>3</sub> target were synthesized using stoichiometric bulks. The SrTiO<sub>3</sub> target obtained by mixing Titania and Strontium oxide (SrO) powder in following molar ratios (SrO : TiO<sub>2</sub>) = (1 : 1). In addition, the CaTiO<sub>3</sub> target was mixed Titania and Calcium oxide (CaO) powder in following molar ratios (CaO : TiO<sub>2</sub>) = (1 : 1). These mixture were pressed at 60 kN for 20 min. The substrates to target distance was 20 mm. The atmosphere in chamber was nitrogen with this pressure was

40 mTorr. A focused Nd:YAG laser (wavelength = 355 nm) was irradiated to the target bulk for 60 min. The films were amorphous, therefore these films were annealed at 1273 K for 10 h for crystallization<sup>[4]</sup>. The crystalline of the film was characterized using X-ray diffraction (XRD). The energy gap of the film was measured by transmission measurement. The gas generation efficiency by decomposition of water in a quartz cell were measured using Xe lamp.

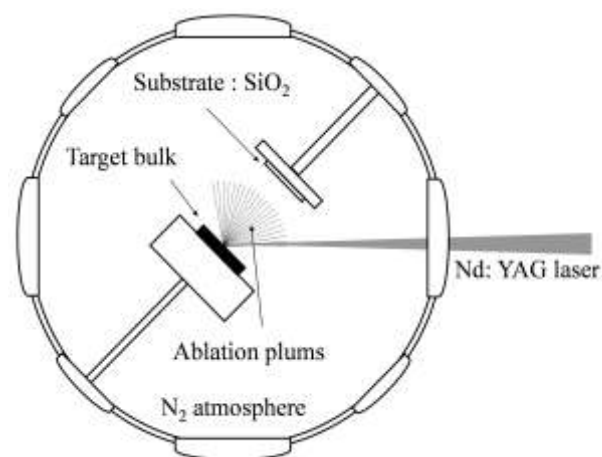


Figure 1 Experimental apparatus for the PLD

#### 3. Results and Discussion

Figure 2 shows XRD patterns of the SrTiO<sub>3</sub> thin films. As can be seen from the graph, annealed thin film was improved crystallinity, and confirmed the theoretical value at the peak. Figure 3 shows XRD patterns of the CaTiO<sub>3</sub> thin films. As can be seen from the graph, annealed thin film was

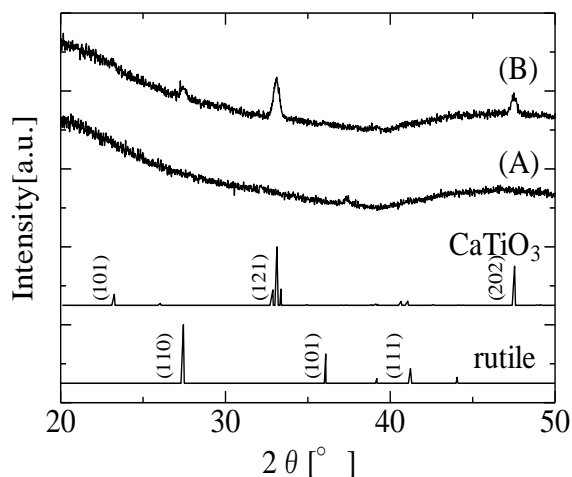


Figure 3 XRD patterns of  $\text{CaTiO}_3$   
(A);asdeposition,(B);postanneal

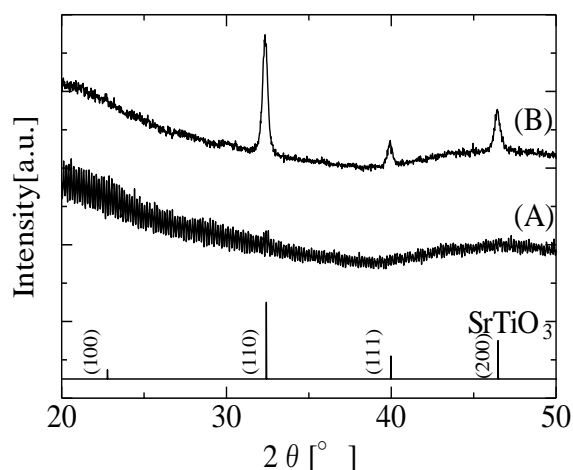


Figure 2 XRD patterns of  $\text{SrTiO}_3$   
(A);asdeposition, (B);postanneal

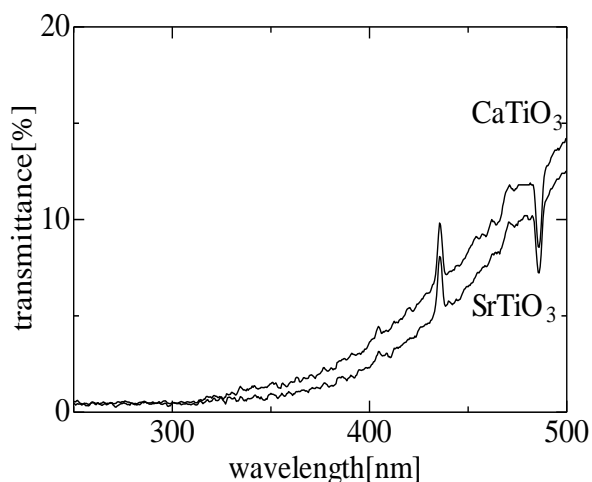


Figure 4 transmittance of thin films

improved crystallinity, and confirmed the theoretical value at the peak.  $\text{CaTiO}_3$  thin films confirmed the peak of  $\text{TiO}_2$ , improvement such as changing the composition ratio and changing the laser wavelength are needed. Figure 4 shows transmittance of  $\text{SrTiO}_3$  and  $\text{CaTiO}_3$  thin films. Comparison of  $\text{SrTiO}_3$  graph and  $\text{TiO}_2$  graph, absorption rate was higher for the  $\text{SrTiO}_3$  thin film. Although not listed in figure, the result of transmission measurement,  $\text{SrTiO}_3$  energy gap was 3 eV, and  $\text{CaTiO}_3$  energy gap was 3 eV. Moreover, gas generating efficiency of  $\text{SrTiO}_3$  was measured  $11 \mu\text{l}/\text{cm}^2/\text{h}$ , and that of  $\text{CaTiO}_3$  was measured  $26 \mu\text{l}/\text{cm}^2/\text{h}$ . Comparison of  $\text{SrTiO}_3$  thin film and  $\text{CaTiO}_3$  thin film, gas generating efficiency of  $\text{CaTiO}_3$  thin film was higher.

#### 4. Conclusion

Was successful in each deposition,  $\text{CaTiO}_3$  from the results of XRD has become mixed crystal with rutile crystal of Titania, the selection of laser components or changing the composition ratio of the bulk, and other assistance necessary to consider there.  $\text{SrTiO}_3$  gas generating efficiency was measured  $11 \mu\text{l}/\text{cm}^2/\text{h}$ , and  $\text{CaTiO}_3$  was measured  $26 \mu\text{l}/\text{cm}^2/\text{h}$ . We will be tried IR ablation, plasma assistance, component analysis of evolved gas using gas chromatography.

#### 5. References

- [1] A. Fujishima, K. Honda : "Electrochemical photolysis of water at a semiconductor electrode", Nature Vol.238, pp37-38, 1972
- [2] J. Yoshimura, Y. Ebina, J. Kondo, K. Domen, A. Tanaka J. Phys. Chem. : "Visible light-induced photocatalytic behavior of a layered perovskite-type rubidium lead niobate,  $\text{RbPb}_2\text{Nb}_3\text{O}_{10}$ ", Vol.97, No.9, pp1970-1973, 1993
- [3] T. Takata, K. Shinohara, A. Tanaka, M. Hara, J.N. Kondo, K. Domen : "A highly active photocatalyst for overall water splitting with a hydrated layered perovskite structure", J. Photochem. Photobiol., A, Vol.106, pp45-49, 1997