

Synthesized of Photocatalytic $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$ Thin Film for Hydrogen Generation by Pulsed Laser Deposition

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Under ultraviolet-light irradiation, photocatalytic reaction using a TiO_2/Pt generates hydrogen that is a renewable energy. However, hydrogen generation efficiency is a small amount, thus we improve the efficiency. According to our previous research, La heavy doped TiO_2 film is efficient in water decomposition. Ca atom is higher hole-effect than La atom. Hence, we synthesize TiO_2 of photocatalytic thin films doped La and Ca on a quartz substrate by pulsed laser deposition. We call that thin films $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$ ($x = 0.0$ to 1.0). Effect of doping impurity such as La and Ca to the hydrogen generation is measured. $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$ targets are mixed La_2O_3 , CaO and TiO_2 powder in following ratios $[(\text{CaO})_x : (\text{La}_2\text{O}_3)_{(1-x)/2}] = (10 : 0)$, $(9 : 1)$, $(7 : 3)$, $(5 : 5)$, $(3 : 7)$ and $(1 : 9)$. The crystallization of the film is measured by X-Ray diffraction. The hydrogen generation efficiency of the film is measured. As a result, the best of crystallization is $(7 : 3)$, then generated gas efficiency is $16.5 \mu\text{l} / \text{cm}^2 / \text{h}$.

1. Introduction

Semiconductor generates electron and hole under irradiation light of more than that's energy gap, which develop oxidation-reduction reaction on semiconductor surface. TiO_2 is frequently used as photocatalyst due to strong oxidation. TiO_2/Pt generates hydrogen⁽¹⁾ under irradiation ultraviolet light with Honda-Fujishima Effect. Energy depletion is inhibited hydrogen, such as renewable energy, however, photocatalytic reaction is inefficient. Previously, $\text{La}_2\text{Ti}_2\text{O}_7$ ^{(2) (3)}, a perovskite structure, and effect of doping alkaline-earth metal⁽⁴⁾ that is higher hole-effect than La have been studied activation.

In this paper, we report photocatalytic reactions on CaTiO_3 , a perovskite structure, and effect of doping La. Moreover, we research in thin film for recycling it since photocatalytic material is usually researched powders, which is difficult to retrieve.

2. Methods

Figure 1 shows the schematic diagram of pulsed laser deposition (PLD) system. $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$ thin films were deposited on quartz substrates under N_2 atmosphere (0.4 mTorr) by PLD. A focused Nd : YAG laser (300 mJ / pulse, 266 nm) was irradiated to the $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$ target bulks for 60 min. as a laser ablation source. The target bulks were mixed CaO , La_2O_3 and TiO_2 powders in following ratios $[(\text{CaO})_x : (\text{La}_2\text{O}_3)_{(1-x)/2}] = (10 : 0)$, $(9 : 1)$, $(7 : 3)$, $(5 : 5)$, $(3 : 7)$ and $(1 : 9)$. The mixed powders were pressed at 80 kN for 40 min. and formed sharp bar as a PLD target. Since the deposited films were amorphous, they were after annealed

at 1273 K for 10 h. The crystallization of the films was measured by X-ray diffraction (XRD). The energy gap of the films was measured by transmission measurement. The hydrogen generation efficiency of films was assessed by water decomposition in the quartz sell for 10 h. using Xe lamp ($100 \text{ mW} / \text{cm}^2$). The pH of water was measured by a pH meter.

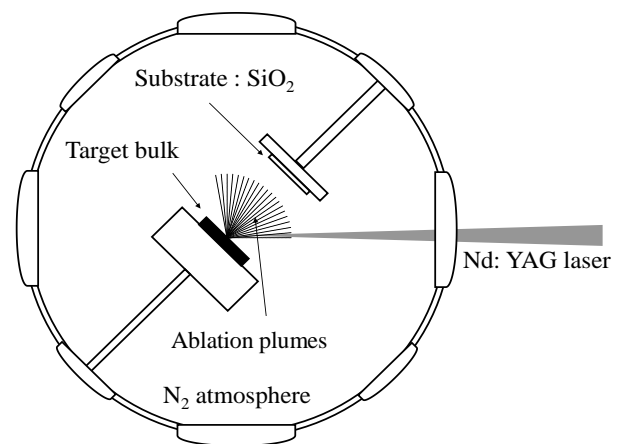


Figure 1. Pulsed Laser Deposition

3. Results and Discussion

Figure 2 shows XRD patterns of the $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$ thin films. As can be seen from the graph, all patterns confirm crystallization of CaTiO_3 or $\text{La}_2\text{Ti}_2\text{O}_7$, a perovskite structure, because there are some peaks which is theoretical value of CaTiO_3 and $\text{La}_2\text{Ti}_2\text{O}_7$. Especially, XRD pattern of $(7 : 3)$ has a sharp peak, thus $(7 : 3)$ is the best of crystallization of all.

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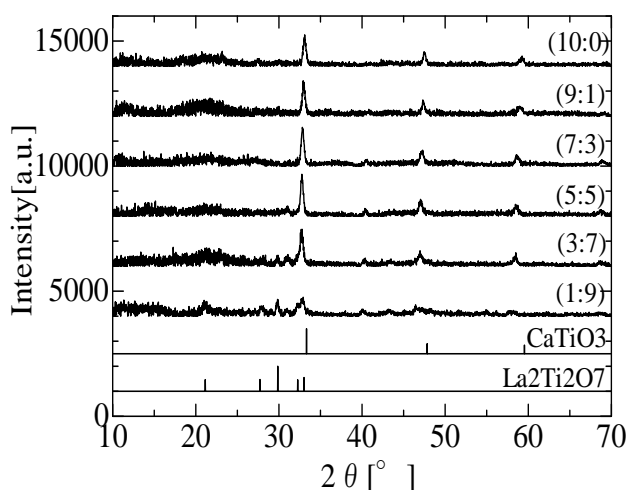


Figure 2. XRD patterns of $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$

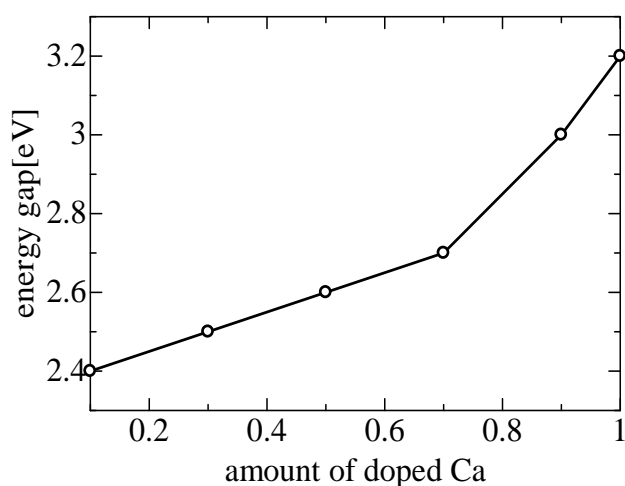


Figure 3. Energy gap of $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$

The energy gap of the $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$ thin films is shown in Figure 3. Decreasing amount of doped Ca atom decreases the energy gap due to impurity level which is generated by doped Ca and La atoms. Therefore absorption band of light was spread toward visible area, and then photocatalytic reaction efficiency may be increased.

The generated gas efficiency and the variation pH are shown in Figure 4. The two graphs are nearly form and same results that the best efficient decomposition ratio is (9 : 1). However, in comparison with XRD patterns, decomposition efficiency of (7 : 3) should have been the most efficient of all. This discrepancy is due to the variation energy gap, thus generation gas efficiency cannot be explained in only term of crystallization.

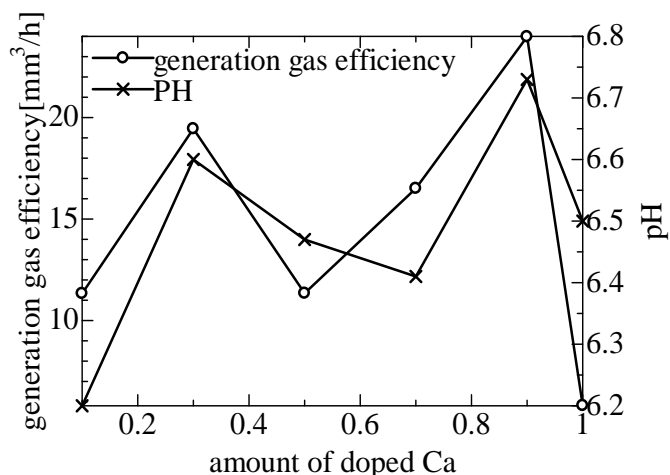


Figure 4. Generation gas efficiency and variation pH of $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$

4. Conclusion

Deposited $\text{Ca}_x\text{La}_{1-x}\text{TiO}_3$ is succeeded by PLD. After annealing, XRD patterns show that the best crystallization ratio is (7 : 3) by XRD. Increasing amount of doped Ca atom increases the energy gap of films. The result of generated gas efficiency and variation pH show the best water decomposition ratio is (9 : 1).

As a result, the best ratio is (9 : 1) in consideration of XRD patterns and energy gap.

5. Reference

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